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MANUAL METHODS FOR SAMPLING AND ANALYSIS OF PARTICULATE EMISSIONS FROM MUNICIPAL INCINERATORS

John T. Funkhouser, et al

Arthur D. Little, Incorporated

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16. ABSTRACT

Municipal incinerators, and similar stationary sources, though contributing only a few percent of the total national air pollution load, are important sources of pollution near population centers. The particulate matter they emit has a significant adverse effect on health, on materials of construction and on visibility; they are responsible for many complaints. Therefore, the Federal Government, through the Environmental Protection Agency, has promulgated standards that specify the permissible levels of particulate matter emitted from newly constructed incinerators operating at or above a charging rate of 50 tons per day. In many cases, however, the chemistry of the particulate species present in these emissions is not well know. Consequently, there is a need to define more thoroughly the chemical nature of particulate emissions from incinerators and to gain a better understanding of how the sample collection equipment used by the EPA influences the physical and chemical properties of the particulate. The primary goal of the program has been to help develop the data base and the technology which will permit representative measurements of source particulate emissions to be obtained from waste incineration sources, and from the particulate pollution control devices associated with such sources.

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This program was conducted by two organizations--Arthur D. Little, Inc., having the primary responsibility with Walden Research Corporation being a sub-contractor. Although Walden had an explicit assignment to carry out the field sampling program, their contribution extended well beyond this role.

During the course of this program, there were two staff members of the Environmental Protection Agency who were primarily involved in the direction of this program. We are indebted to John Burckle and Robert Larkin (now associated with the National Institute for Occupational Safety and Health) for their support, cooperation and direction to this program.

FOREWORD

Airborne particulate matter is a major air pollutant having significant effects on health, economics, ecology, visibility, and aesthetics. Effective techniques and hardware systems for source emission measurements are required for application to the various emitting sources to achieve control of particulate emissions and protect the environment.

This contract work was sponsored by the National Environmental Research Center at the Research Triangle Park, North Carolina, to review methods applied to the measurement of particulate emissions emanating from incinerators and, in particular, investigate the validity of the EPA sampling train.

While today's incinerators contribute only a small portion of the total particulate burden in the Nationwide Emission Inventory, this portion is emitted in close proximity to urban centers. Further, recent studies on solid waste disposal practices indicate an increase in incineration practices in urban centers. The facts leading to this conclusion are given as:

...Urban areas now account for some 50% of the U.S. population with the trend for centralization increasing

...The rate of production of urban wastes is estimated to be about 8.5 pounds per capita per day and increasing annually at about 4% per capita

...Landfill sites for major urban centers are rapidly disappearing and alternatives to volume reduction through thermal processing are not practiced to any significant extent.

This report is included in the Environmental Protection Technology series - the series, devoted to new or improved technology required for control and treatment of pollution sources to meet environmental quality goals, includes reports of work dealing with research, development, and demonstration of instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution.

John O. Burckle
Project Officer
U.S. Environmental Protection Agency
Office of Research & Development

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1. SUMMARY

1.1. PURPOSE AND SCOPE

In response to growing public demands for clean air, the Federal Government is expending considerable effort to identify sources of air pollution and appropriate abatement procedures to control these sources. Municipal incinerators, and similar stationary sources, though contributing only a few percent of the total national air pollution load, are important sources of pollution near population centers. The particulate matter they emit has a significant adverse effect on health, on materials of construction and on visibility; they are responsible for many complaints. Therefore, the Federal Government, through the Environmental Protection Agency, has promulgated standards that specify the permissible levels of particulate matter emitted from newly constructed incinerators operating at or above a charging rate of 50 tons per day.

In many cases, however, the chemistry of the particulate species present in these emissions is not well known. Furthermore, because sampling and analytical methods have not been scientifically documented, methods commonly used may not adequately consider the physical and chemical changes that can occur in the assay process and thus lead to the formation of what is expressed empirically as "false particulate." Therefore, the results that are presently obtained may not truly reflect the particulate burden to the atmosphere. Consequently, there is a need to define more thoroughly the chemical nature of particulate emissions from incinerators and to gain a better understanding of how the sample collection equipment used by the EPA influences the physical and chemical properties of the particulate.

The primary goal of the program has been to help develop the data base and the technology which will permit representative measurements of source particulate emissions to be obtained from waste incineration sources, and from the particulate pollution control devices associated with such sources. One of the prime requirements for these measurements is that they reflect, as accurately as possible, the particulate burden on the ambient air. Thus, it will be necessary to develop standard methods which are sufficiently well documented to be applied in the field to new and unfamiliar situations. Our part in this overall process was to help develop a practical working understanding of the complex physical and chemical interactions during sampling that lead to the formation of particulates.

1.2. APPROACH

To accomplish this goal, we:

- Prepared an information base describing incineration processes, sampling methodology, and procedures;

- Delineated the technical requirements necessary to meet the program objectives;
- Evaluated existing methods in terms of these requirements to determine their strengths and weaknesses;
- Filled in gaps in knowledge and understanding by reviewing the literature and speaking with people knowledgeable in the field;
- Prepared a plan to characterize the emissions through field tests and laboratory evaluations; and
- Performed the required field tests, using the sampling train designated by EPA, and evaluated results.

1.3. FINDINGS AND CONCLUSIONS

Our findings and conclusions can be grouped into categories relating to sampling procedures, nature of the particulate catch, and potential errors. They are summarized below along with unanswered questions associated with each of these categories that remained unanswered at the completion of this program.

1.3.1. Sampling Procedures

- In our sampling runs, the EPA sampling train caught more than 80% of the particulate catch in the probe/cyclone and filter.

  Question: *How does process cycle variation influence this distribution?*

- The probe/cyclone collects a significant proportion of the particulate.

  Question: *How does particulate size distribution affect this? What is the influence of having the cyclone-filter arrangement inside the stack?*

- For incinerator particulate catch, little change in mass seems to occur with aging of the sample.

  Question: *Is this true for a wide variety of incinerators or just the two studied under this program?*

- Very little of the material caught in the impingers is related to what is normally considered particulate.

  Question: *In the case of incinerator sampling, do the impingers have any role in the EPA train except to protect the meters and pumps?*

- **The measurement of impinger catch by means of weight may be inappropriate.**

  Question: *If the impinger catch is important, titration for acid equivalent or determination of chloride and sulfate should be considered as an alternative approach for incinerator sampling.*

1.3.2. Nature of Particulate Catch

- **The "front half" catch is almost totally inorganic mineral particulate.**

  Question: *How does composition vary with particle size? How does the composition of condensible fraction vary with temperature of collection?*

- **The impinger catch is essentially mineral acid.**

  Question: *Even though the mass of mineral particulate in the impingers is low, do significant quantities (number basis) of "fines" collect there?*

1.3.3. Potential Errors in Sampling and Analysis

- **The use of Drierite to "dry" the particulate catch may lead to erroneous results.**

  Question: *What are proper conditions for measurement of filter catch?*

- **With the possible exception of sulfates, there seemed to be little false particulate formed in the "front half" of the sampling train.**

  Question: *What sampling train arrangements and materials of construction are needed to ensure that this does not become a problem?*

- **Based on our findings, it is not clear whether the oxidation of SO_2 in the sampling train is a potential source of error in the impinger catch.**

  Question: *To what extent is this a problem, and what needs to be done to eliminate it or keep it to a minimum?*

- **Particulate catch is defined as all material other than uncombined water which exists as a finely divided liquid or solid at standard conditions.**

  Question: *Does the EPA train meet this definition? Would the use of a dilution cooling system or other procedures do a better job?*

2. BACKGROUND

When attempting to adequately sample a complex effluent stream such as the emissions from a municipal incinerator, it is important to understand the situation in which the measurements were taken. As a result of the complexity of the feed material and the difficulties in obtaining complete combustion, incinerator emissions themselves are very complex and variable. This is true for both the particulate* and the gaseous emissions, as can be seen from the data presented in Table 1 and the detailed discussion of the nature of the emissions from incinerators given in Appendix A. Some of the factors that influence the nature of these emissions are discussed below.

2.1. REFUSE COMPOSITION

A generalized average composition for the waste that must be handled by a municipal incinerator is shown in Table 2. As the composition of the waste changes, the emissions can be affected. For instance, the percentage of the ash carried over usually ranges between 10 and 20% of the total available in the refuse so the ash content of the refuse is a major factor in determining emission rates. As shown in Table 3, the ash content of incinerated material will vary widely from a few percent (newspaper, polyethylene film, etc.) to quite high (rubber tape, shoe leather, filled plastics, etc.). Other factors associated with the character of the refuse are volatile metals content and volatile combustible content. As either of these increases, more emissions may be observed. A large volume of combustible rich pyrolysis gas generated during the incineration of refuse with a high volatile content tends to result in particulates with a high fraction of soot and other combustibles.

2.2. THE INCINERATOR

The incinerator furnace provides the environment for controlled combustion of solid wastes in air. The furnace usually includes grates to support the burning material within a refractory or other enclosure. The refuse is processed by controlled oxidation, with liberation of heat, that produces flue or combustion gases and a residue or ash. The refuse to be processed in the furnace must be fed at controlled rates with suitable material handling equipment. The ash residue must be removed and transported in bulk to a disposal area, while the effluent flue gases must be removed and delivered to the stack or chimney after suitable treatment for control of air pollution.

---

*Particulates are defined as any material, other than uncombined water, which exist as a finely divided liquid or solid at standard conditions (70°F and 1° atm.). See Federal Register, 36, No. 247, Part II, 24876-24895 (December 23, 1971).

TABLE 1

Composition of Incinerator Emissions*

Component	Concentration Levels		
	%	ppm	lb/ton refuse
Nitrogen	60-65	---	---
Water	10-30	---	---
Oxygen	10-15	---	---
Carbon Dioxide	3-5	---	---
Carbon Monoxide	---	40-500	3-35
Sulfur Oxides (SO_2)	---	30-60	2-4
Nitrogen Oxides (NO_2)	---	15-50	1-3
Hydrocarbons	---	15-50	1-3
Hydrochloric Acid	---	10-40	1-2
Particulate	---	1 grain/SCF	6-10

*A summary of literature values, see Appendix A.

TABLE 2

Average Refuse Composition--As-Discarded Basis*

Category	Weight (%)	Description
Glass	8.3	Bottles (primarily)
Metal	8.2	Cans, Wire, Foil
Paper	35.6	Various Types, Some with Fillers
Plastics	1.1	Polyvinyl Chloride, Polyethylene, Styrene, etc., as Found in Packaging, Housewares, Furniture, Toys and Nonwoven Synthetics
Leather & Rubber	1.5	Shoes, Tires, Toys, etc.
Textiles	1.9	Cellulosic, Protein, and Woven Synthetics
Wood	2.5	Wooden Packaging, Furniture, Logs, Twigs
Food Wastes	23.7	Garbage
Miscellaneous	1.7	Inorganic Ash, Stones, Dust
Yard Wastes	15.5	Grass, Brush, Shrub Trimmings
	100.0%	

*ADL estimate--from "Systems Study of Air Pollution from Municipal Incineration," a report to NAPCA (now EPA) under Contract CPA-22-69-23.

TABLE 3

Ash Content of Selected Industrial and Municipal Wastes*

Ash Content (%)	Material
0-2	Polyethylene film, draft paper, waxed milk cartons, vegetable food wastes, semi-cured tubes, nylon fabric and yarn, newspaper
2-5	Banbury rubber scrap, vinyl scrap, plastic-coated paper, lawn grass, balsam spruce, ripe tree leaves, cooked meat scraps
5-10	Vinyl-coated fabric, expanded Ensolite, uncured frictional duck, cured flash and molded goods
10-15	Vinyl-coated felt, raw batch stock, junk mail, wire-braid hose
20-25	Shoe leather, rubber-coated fabric, cloth uppers, ensolex trim, trade magazines
25-30	Foam scrap, heel and sole composition
<30	Cloth-backed foam, die strip, rubber tape

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*"Systems Study of Air Pollution from Municipal Incineration," a report to NAPCA (now EPA) under Contract CPA-22-69-23.

The feeding of the refuse may be either batch or continuous, although the recent trend has been toward the use of continuous firing to improve process control. In most cases, refuse is batch fed directly into the furnace with a clam-shell bucket or grapple attached to a traveling crane; the rate of feed is controlled by the time cycle and the degree of bucket loading. In a few plants, a front-end loader operating on a paved floor charges the furnace.

A ram-type feeding device is sometimes used for controlled feeding. With such a system, either the ram can clear the hopper at each stroke or an oversize hopper can be filled with refuse and the ram used to shear a horizontal section of refuse at selected intervals. The ram feeder provides an air seal at the feed to the furnace--an improvement over the bucket or the front-end loader systems of batch feeding, which usually let in undesirable quantities of cold air, as well as releasing occasional puffs of flames or hot gases, while the charging gate is open. The inrush of cold air can be detrimental to the inside refractory walls of the furnace and can cause smoke evolution by cooling and quenching the burning process.

Newer designs for incinerator systems nearly always specify continuous feeding of refuse to the incineration furnace. Continuous feeding can be accomplished by means of a hopper and a gravity chute; a mechanical feeder, such as a pusher, ram, rotary feeder, or the like, which can be filled directly from a hopper supplied with refuse by a bucket and crane; a front-end loader from a feeding floor, a conveyor transporting the refuse from the receiving area; or an air injection system (shredding with suspension burning).

The most frequently used system is the hopper and gravity chute. A rectangular hopper receives the refuse delivered by the crane and bucket. The bottom of the hopper terminates in a rectangular chute leading downward to the furnace grate or other feeder conveyor at the entrance to the furnace chamber itself.

If suspension burning is to be employed in the incinerator furnace, the refuse should be prepared by suitable shredding or grinding, and the most desirable feeding method is air injection. Suspension burning has been used successfully in waterwall boilers for the generation of steam from waste products such as wood bark, bagasse, and similar materials. In conformance with practices in the fossil-fuel-fired boiler industry, shredded refuse can be air injected for corner firing, for spreader firing, or for "cyclone" firing--all of which are in commercial use for the generation of steam from powdered or crushed bituminous coal. With suspension burning, a burn-out grate is provided at the bottom of the water-wall furnace chamber to permit larger particles or slow-burning materials to burn completely.

A more comprehensive description of the incineration process is given in Appendix B, but even from the above it should be clear that to permit interpretation of particulate emission data, as many known and suspected incinerator variables as possible should be recognized. Some of these variable are:

- Incinerator Type: Batch, continuous grate or rotary kiln.

- Grate Type: The grate type (plus charging method--batch or continuous) often defines the general design of the total furnace system. Stoking intensity (causing attrition of the residue) varies widely between systems and would be expected to increase the fraction of the ash material in the size range capable of suspension and to expose more of this suspendable material to the undergrate air flow. The percent open area of the grate surface controls the amount of ash material dropping through the grate (siftings). This grate parameter varies widely (2-30%). Since the small-particle-size ash is "lost" from the bed by this mechanism, less is available for suspension in the undergrate air flow.

- Batch Size, Method, and Batch Frequency in Batch Units: Emissions will vary greatly with these variables. Sampling duration and timing will be critical considerations.

- Combustion Chamber Design: Furnace design will affect mixing patterns, particle settling, etc.

- Incinerator Size: Increasing the size of incinerator units from 3 to over 100 TPD has been shown to result in higher emission rates, but the effect of size on emission factors has not been established quantitatively over the more practical size range for municipal furnace units (50-300 TPD).

- Burning Rate: It is expected that higher emission rates will be encountered at higher burning rates.

- Undergrate Air Velocity: Ash particles may be entrained when the velocity of the gases through the fuel bed exceed the terminal velocity of the particles. Undergrate air velocities typically vary from a minimum of 10 SCFM/ sq. ft. of grate area to 100 SCFM/ sq. ft. On the basis of the terminal velocity, particles up to 70μ (equivalent diameter) are expected to be entrained at the lowest velocities and up to 400μ at the highest. One systematic study of the effects of underfire air, secondary air, excess air, charging rate, stoking interval, and fuel moisture content on the emission rate from an experimental incinerator has led to the conclusion that the velocity of the underfire air was the variable that most strongly influenced particulate emission rate.

2.3. PARTICULATE CHARACTERISTICS AND EMISSION MECHANISMS

Particulate incinerator emissions occur mainly by the following mechanisms:

- The mechanical entrainment of particles from the burning refuse bed;
- The cracking of pyrolysis gases; and
- The volatilization of metallic salts of oxides.

The first of these mechanisms is favored by refuse with a high percentage of small-particle low-density ash, by high underfire air velocities, or by other factors that induce a high gas velocity through the bed. The second mechanism is favored by refuse with a high volatile content that produces pyrolysis gases with a high carbon content, and by conditions above the fuel bed that prevent the burnout of the coked particles formed by the cracking of the volatiles. The third mechanism is favored by high concentration of metals that form low-melting-point oxides and by high temperatures within the bed.

Two major types of particles are:

- Mineral particulate --the incombustible fraction of fly ash; and
- Combustible particulates--the char and soot produced by the thermal cracking, and condensed organic vapor (white smoke).

A generalized summary of the incinerator emission rates for a variety of pollutants is given in Table 4.

2.4. NON-PARTICULATE EMISSIONS

The analytical methodology employed for determining particulates must take into account the influence of gaseous emissions, such as condensible hydrocarbons and organic acids. The values shown in Table 4 are "typical" for some of these materials. These typical values, however, will not remain constant. For example, hydrochloric acid content is expected to quadruple by the year 2000 because of an increase in polyvinyl chloride resins (Table 5).

2.5. INFLUENCE OF AIR POLLUTION CONTROL EQUIPMENT

Although the flue gases from incinerators contain a number of pollutants, most, if not all, air pollution control (APC) equipment installed on existing units addresses the problem of particulate removal. For this purpose, a number of devices are in use, ranging in particulate removal efficiency from 5-15% to upward of 95%.

TABLE 4

Emission Rate Estimates For a Variety of Pollutants*

Pollutants	Amount (lbs/ton of refuse)
Particulates	
Mineral	15
Combustible	4.6
Carbon Monoxide	35
Hydrocarbons	2.7
Specific Organics	
Acids	0.1
Aldehydes	0.2
Polynuclears	0.005
Nitrogen Oxides	3
Sulfur Oxides (total)	3.9
Inorganic Acids	
Hydrochloric Acid	1.5
Hydrofluoric Acid	0.01
Volatile Metals	0.03

*A summary of literature values, see Appendix A.

TABLE 5

Anticipated Growth Patterns of PVS in Average Refuse and Associated HCl Furance Emission Factors*

Year	Plastics in Refuse (%)	PVC Resin in Plsstics (%)	HCL Emission Factor lb HCl per Ton of Refuse
1968	1.1	7.8	0.99
1970	1.3	0.0	1.50
1975	1.8	0.6	2.20
1980	2.7	8.7	2.71
1990	3.5	0.9	4.41
2000	4.2	1.2	5.44

*ADL estimate--from "Systems Study of Air Pollution from Municipal Incineration," a report to NAPCA (now EPA) under Contract CPA-22-69-23.

Settling chambers or expansion chambers have been used in this breeching and flue gas ducts and many of the older installations have employed refractory baffles across the breechings to collect particles. In some instances, a coarse spray of water is directed into the flue gases and toward the baffles with most of the water falling to the floor of the chamber without vaporization. The wet floor and baffles improve particulate removal by preventing re-entrainment of settled ash into the flue gas stream. Dry collectors are usually "cyclones" in which the flue gas particles concentrate on the inside of a cylindrical wall (as a result of centrifugal force) and solids are discharged at the lower end and opposite to the cleaned gas outlet.

Other devices used for particulate removal from flue gases include scrubbers, which may be open spray chambers, packed chambers, or high-pressure drop units (e.g., Venturi scrubbers). Filters used for particulate removal usually are high-temperature fabrics, such as silicone-treated glass fiber cloth, arranged in bags or tubes. Electrostatic precipitators are currently receiving increased attention for particulate removal from incinerator flue gases.

2.6. SAMPLING TRAINS

Procedures and devices should be able to remove a measured representative sample of stack gas and to collect the particulate matter (solid and liquid) which exists in the stack gas plus the potential particulate matter, i.e., material which would condense to an aerosol (free liquid water excepted) as incinerator gases cool by dilution with the ambient atmosphere. The ultimate method should be able to collect particulate and potential particulate matter without introducing any extraneous material that could be misinterpreted.

Classically, stack sampling for particulate pollutants has been directed towards measuring the mass of dust emitted which contributed to dust fall (solid particles in the gas stream >1μm). At present there also is interest in the smaller sizes of particulate (0.1-1.0μm) because they are believed to influence cloud formation in the atmosphere, and atmospheric visibility and haze.

All particulate sampling systems include the following units:

- nozzle
- probe
- collecting device
- metering unit
- suction source

These units are not always independent components of the system; for example, a cyclone is sometimes used to collect particles and meter gas.

The arrangement, both as to location and sequence, is a primary differentiating feature among systems. The design of the sampling system, both as to configuration and size, may depend on the sampling procedure contemplated and the interests of the designer. Most state-of-the-art sampling systems do not collect condensibles, but only particles which are in essence gas-borne solid matter larger than one micron in diameter at conditions existing inside the stack. For a more complete discussion of existing sampling trains refer to Appendix C. A general presentation on sampling for particulates is included as Appendix J.

3. EXPERIMENTAL PROGRAM

Our basic approach to this program was to collect samples in the field in a manner that would permit them to be fully characterized in the laboratory. Thus, in our field work, we endeavored to ensure that the samples were of adequate size and were representative with respect to variations in chemical and physical properties.

3.1. COLLECTION OF FIELD SAMPLES

The sampling format and procedure used during this program was similar to the one published in the Federal Register on December 23, 1971. (A copy is included as Appendix K.) The major difference between our procedure and the published one were related to the fact that we did not sample to determine emission rates but rather only to obtain a qualitatively representative sample of the stack emissions. Therefore, we did not sample the stack on a statistical basis, nor did we correct gas volumes for water vapor, nor did we, therefore, relate emissions to incinerator performance.

The EPA sampling train is shown in Figure 1. Basically, it consists of a nozzle, probe, cyclone, filter and impingers. The material collected in these various components of the sampling train were separated with an eye towards exploring whether different types of particulate matter was preferentially collected by the different parts of the train. Thus, the particulate catch was separated according to probe and cyclone catch, probe washings, filter catch, filter holder washings, impinger catch, and acetone rinse of the impingers.

The criteria for evaluating the EPA sampling train with regards to its ability to adequately collect the particulate matter in the effluent stack gas from municipal incinerators centered on whether:

a. The particulate collected by the EPA train* matched the material defined as particulate by EPA--namely, "anything that is a solid or liquid (other than uncombined water) at 70°F and one atmosphere."

b. The filter acted as an efficient collector of the particulate matter generally classified as inorganic mineral particulate;

c. The impingers collected condensibles;

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*The EPA train currently recommended does not include a cyclone, whereas all of this work was done with a train that included a cyclone.

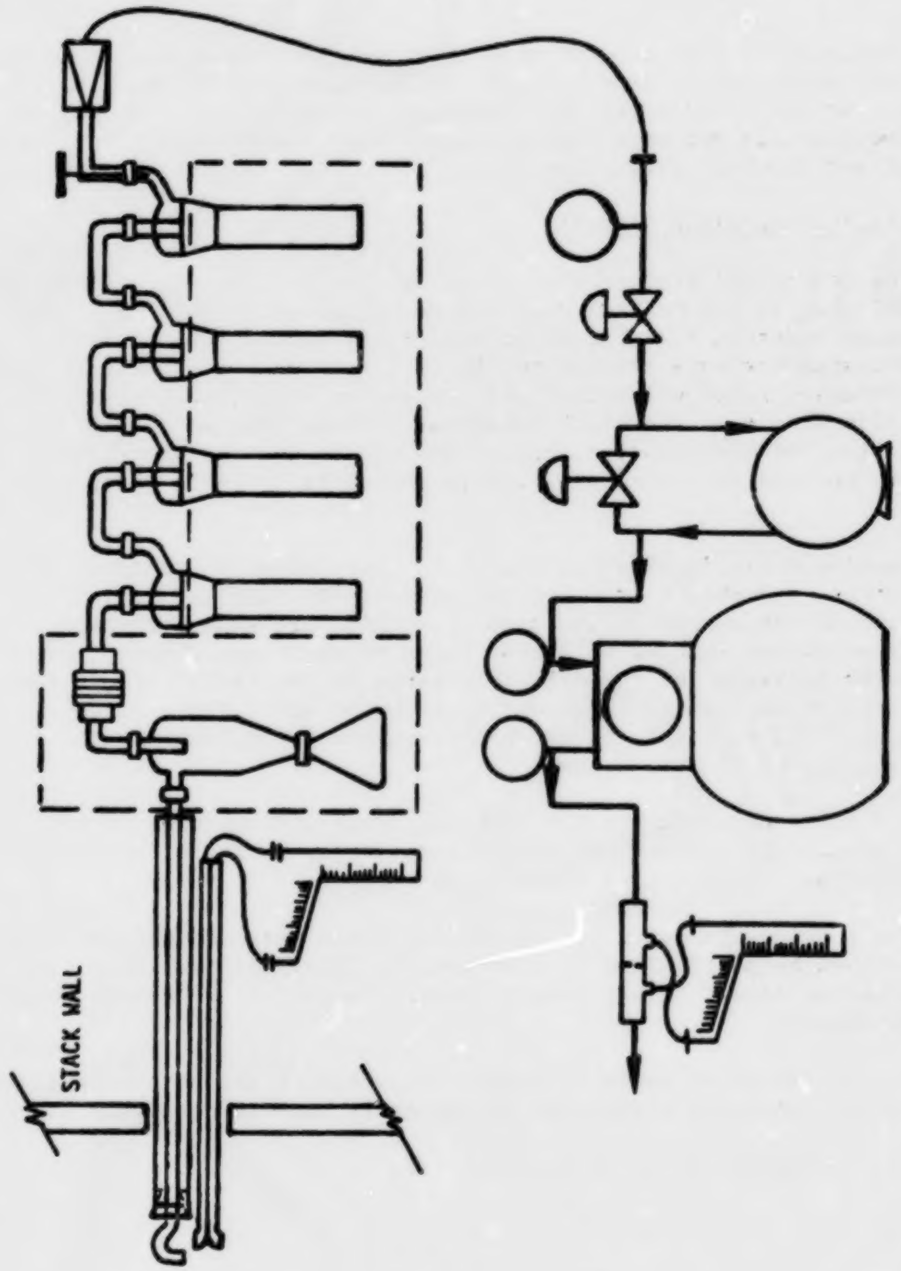

FIGURE 1

EPA Particulate Sampling Train (early version)

d. There were interactions between the sampling train and the sample during its collection; and

e. Interactions between the gas phase and the collected particulate generated false particulate or caused weight losses.

Most of our sampling was conducted at a local 250-tons per day (TPD) triple traveling grate incinerator, which operated continuously from Monday to Friday (samples coded (NI-__). The sampling point selected was in the rectangular duct leading from the wet scrubber to the base of the stack. The duct was 6'6" wide, 16'6" high. The roof of a small shed served as the sample platform and facilitated installation of rails for stabilization and operation of the sample collecting unit. The control module was located inside the shed. In addition, a few runs were made at a local batch incinerator. (These samples were coded BI-__.)

3.2. TABULATION OF SAMPLING RUNS

Eighty-two sampling runs were made during the field program. A complete listing of these runs is given in Appendix D. In summary, these can be categorized as follows:

Type of Experiment	Table in Appendix D	No. of Runs
EPA System Familiarization	D-1	10
Filter Leakage Studies	D-2	6
Filter Leakage Studies	D-3	19
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Collection of Samples for Microscopy Studies	D-5	16
Collection of Samples for Quantitative Analysis and Chemical Characterization	D-6,7	23

3.3. OPERATION OF A COMMERCIAL EPA SAMPLING TRAIN

In order to help in our evaluation of the EPA sampling train, we made several operational tests on a commercially available unit. (Note: the train manufactured by Research Appliance Company was used for this program, but it is likely that other commercially available units provide equivalent performance. This study was not intended to act as a certification of the particular train, but rather to evaluate the general arrangement of the component parts.)

Several tests were conducted to evaluate the apparent inconsistent development of high pressure drop across the sample train during period of sampling which exceeded one hour (see Table 6). For this evaluation, pressure drop was measured as a function of time, volume throughput, and filter loading for several operating procedures.

In the first set of tests, a filter was operated for approximately 3-1/2 hours, with three changes in impinger fluid. In Test 39 (65 minutes), the average sampling rate was 0.93 cfm (0.026 cmm); the initial vacuum was 6.5" Hg and increased to 7.4" Hg. The impinger samples were removed and the impinger recharged. Test 40 (65 minutes) was then conducted at an average rate of 0.92 cfm (0.026 cmm) starting at a pressure of 7" Hg which increased to 16" Hg. The impinger samples were again removed and the impinger recharged. Test 41 (87 minutes) was then carried out in which the vacuum increased to 22" Hg. At the latter condition, the flow was only 0.23 cfm (0.007 cmm). The total sample volume through the filter was 5.12 m^3. Dust loading for this sample as shown in Table 6, was 195.2 mg/m^3.

Two additional tests, 42 and 43, were run at a collection rate of 0.9 to 1 cfm (0.025 to 0.028 cmm) until the vacuum at the pump reached a nominal 20" Hg. Run 42 had an initial vacuum of 7" Hg which is approximately double that usually indicated at the sampling outset. This built up to 14" Hg at the end of the first 65 minutes. On examination, it was observed that silica gel had carried over into the suction line. When the silica gel was removed from the pump suction line and the accumulated water was removed from the two wet impingers, the vacuum dropped back to 8" Hg. The run was continued for another 31 minutes, by which time the pump pressure had reached 21" Hg. Run 43 was carried out in a similar manner with a change in impinger solutions after 7 minutes. After a total elapsed time of 105 minutes, the pump pressure reached 20" Hg. In each of the two tests, 42 and 43, approximately the same amount of incinerator effluent was sampled with the final vacuum in each case being around 20" Hg. Filter loadings were almost identical for these two tests.

Three additional tests, numbers 44, 45, and 46, were made using the same sampling rate as in tests 42 and 43. The results of these tests were similar to those of 42 and 43.

From a review of these results and those from earlier tests, the following conclusions were drawn:

- Careful observations of several tests conducted over the course of a month show no anomalies in the function or behavior of the RAC sampling train.

- Minor variations of 0.5 to 1.0" Hg which may occur in starting vacuums probably are due to variations in the pressure drop across the filter media and the packed silica gel bed.

TABLE 6

RAC Sampling Train Evaluation Data

Date	Run No. (NI-)	Gas Volume (m^3)	Time (min)	Pressure Change ("Hg)	Filter Weight	
					(mg)	(mg/m^3)
7-7	39,40,41	5.12	217	6.5 to 22	989	195
7-15	42	2.35	96	7 to 21	563	240
7-15	43	2.55	105	3 to 20	551	216
7-22	44	2.47	100	3 to 20	---	---
7-22	45	1.49	60	4 to 20	271	182
7-22	46	2.42	93	3 to 16	563	198

- The pump vacuum can be directly related to the mass of particulate matter collected on the filter and the sampling rate.

- A sampling rate of 0.9 to 1.1 cfm (0.025 to 0.031 cfm) can generally be maintained until pump vacuum increases to 18" Hg; it then becomes difficult to maintain this flow.

- Longer periods of sampling can be achieved at lower sampling rates if coverage of a long-time burning cycle is desired.

- For the "normal" particulate loading of the effluent at the incinerator tested, a sampling rate of 1 cfm (0.028 cmm) can usually be maintained for only about 90 minutes in which time filter loading is about 5 mg/cm^2 and pump vacuum has increased to about 20" Hg.

3.4. CHARACTERIZATION TECHNIQUES

A variety of analytical techniques is available to characterize the collected particulates with respect to their chemical and physical properties. Figure 2 illustrates how these options were considered for this program. Although all techniques were tried during this program (with the exception of fluorescence and liquid column chromatography) because of the low levels of organics, the most useful information was developed via those techniques which were most applicable to inorganic materials. Qualitative information was obtained utilizing x-ray techniques, emission spectroscopy, and wet chemical techniques. Figure 3 illustrates the sequence followed for quantitative data.

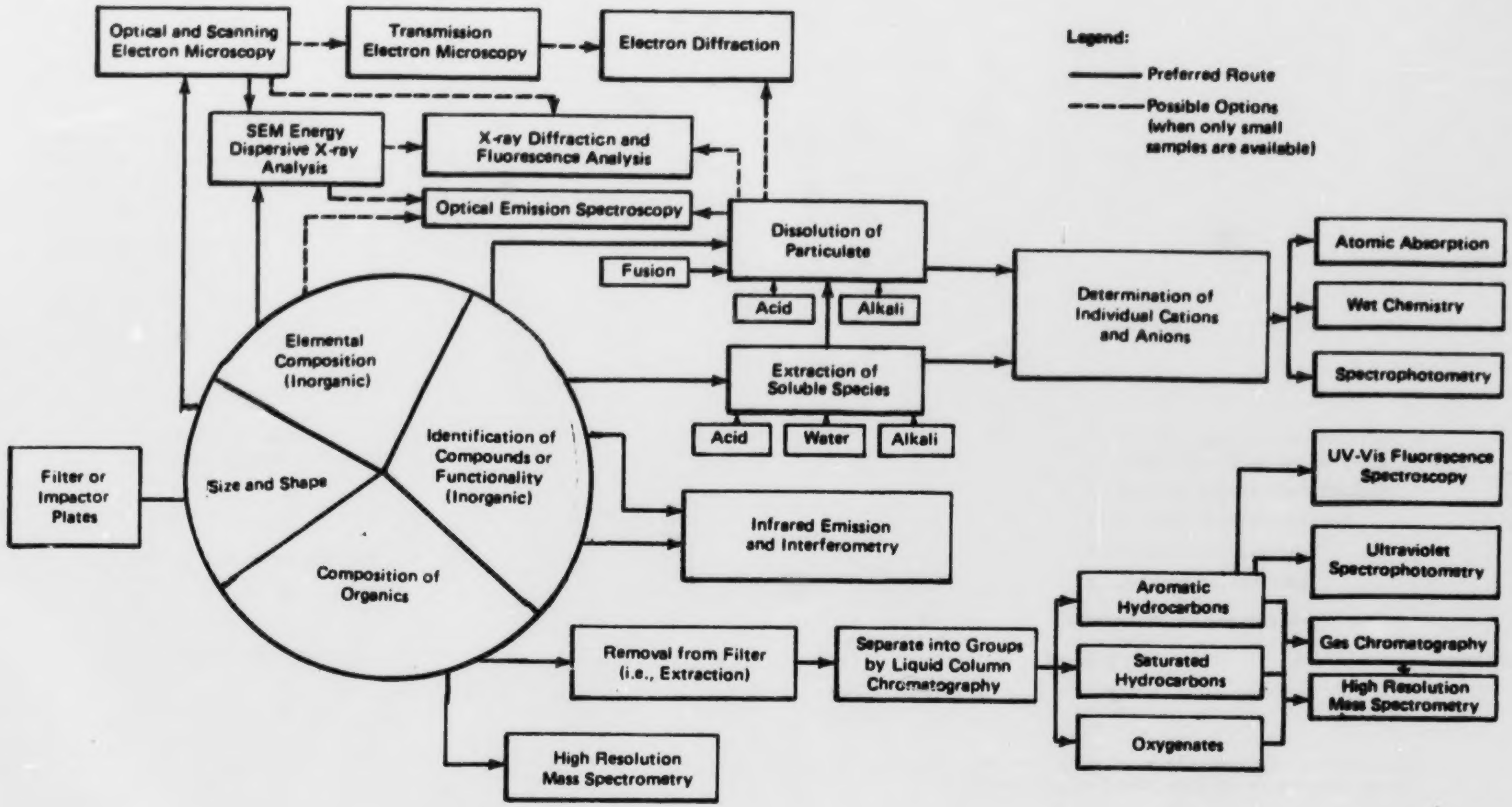
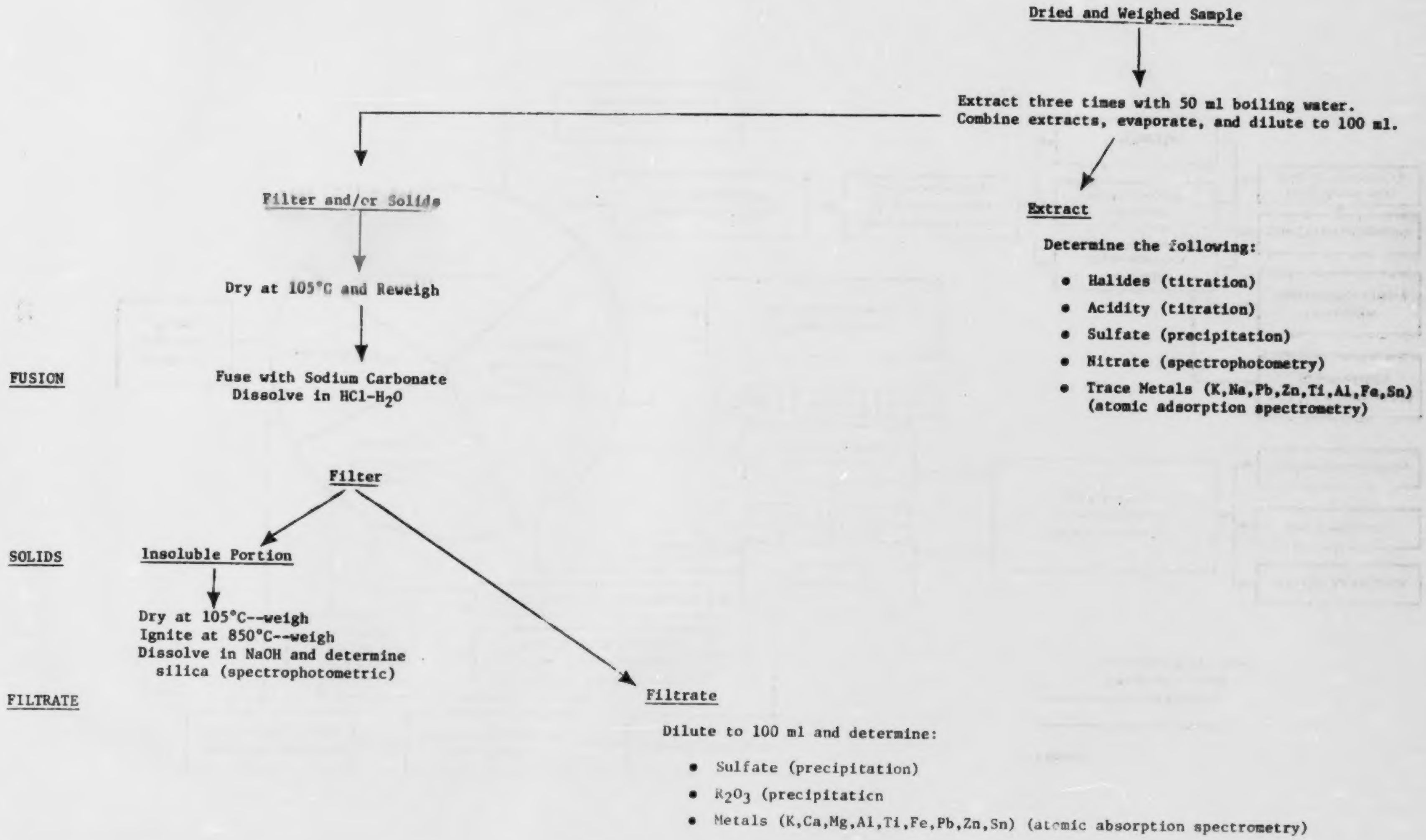

Optical and Scanning Electron Microscopy
Transmission Electron Microscopy
Electron Diffraction
Legend:
Preferred Route
Possible Options (when only small samples are available)
SEM Energy Dispersive X-ray Analysis
X-ray Diffraction and Fluorescence Analysis
Optical Emission Spectroscopy
Dissolution of Particulate
Fusion
Acid
Alkali
Determination of Individual Cations and Anions
Atomic Absorption
Wet Chemistry
Spectrophotometry
Extraction of Soluble Species
Acid
Water
Alkali
Filter or Impactor Plates
Elemental Composition (Inorganic)
Size and Shape
Identification of Compounds or Functionality (Inorganic)
Composition of Organics
Infrared Emission and Interferometry
UV-Vis Fluorescence Spectroscopy
Ultraviolet Spectrophotometry
Aromatic Hydrocarbons
Saturated Hydrocarbons
Oxygenates
Gas Chromatography
&
High Resolution Mass Spectrometry
Removal from Filter (i.e., Extraction)
Separate into Groups by Liquid Column Chromatography
High Resolution Mass Spectrometry

FIGURE 2

Flow Chart for Examination of Collected Particulate

FIGURE 3

Analysis of Solid Catch



Dried and Weighed Sample
FUSION
SOLIDS
FILTRATE
Filter and/or Solids
Extract
Filter
Insoluble Portion
Filtrate

Extract three times with 50 ml boiling water.
Combine extracts, evaporate, and dilute to 100 ml.

Extract

Determine the following:

- Halides (titration)
- Acidity (titration)
- Sulfate (precipitation)
- Nitrate (spectrophotometry)
- Trace Metals (K,Na,Pb,Zn,Ti,Al,Fe,Sn) (atomic adsorption spectrometry)

Dry at 105°C and Reweigh

Fuse with Sodium Carbonate
Dissolve in HCl-H_2O

Dry at 105°C--weigh
Ignite at 850°C--weigh
Dissolve in NaOH and determine silica (spectrophotometric)

Dilute to 100 ml and determine:

- Sulfate (precipitation)
- R_2O_3 (precipitaticn
- Metals (K,Ca,Mg,Al,Ti,Fe,Pb,Zn,Sn) (atcmic absorption spectrometry)

4. PROGRAM RESULTS

Detailed discussions of the experimental findings obtained during this program are presented in Appendices E, F, G and H. A condensed overview of these findings is given in the following discussion.

4.1. CHARACTER OF THE PARTICULATE CATCH FOUND IN THE "FRONT HALF" OF THE SAMPLING TRAIN

Table 7 shows the distribution of the particulate catch in the EPA sampling train. As can be seen from this data and that in Table 8, the total material caught in the probe/cyclone/filter was remarkably consistent, both between incinerators and seasons. Only a small portion of the total particulate catch was found in the impingers. (With but one exception, 20% or less was caught in the impingers.) Because of program limitations, we did not make any effort to explain the variations between incinerators (NI vs. BI) or amount collected in the probe/cyclone. The fact that the probe/cyclone collected almost twice as much material in October as in the spring may be related to the composition of the refuse; that is, it led to more particles greater than five microns, which were then collected in the cyclone rather than the filter. Because the EPA train no longer utilizes a cyclone, this type of difference does not appear important.

Small quantities of organic material could be found by extraction, but total organic matter on the filter amounted to less than 5% of the filter catch. (When coupled with the organic matter in the impingers, total organics were estimated to be always less than 10% of the total catch.)

Overall summaries for the composition of the probe/cyclone and filter catches are given in Table 9. The principal cation components (>5% of total cations) of the mineral particulate common to both the probe/cyclone and filter catch were: zinc, lead, potassium, and sodium. In addition, iron, titanium, and aluminum were present in both but were relatively much higher in the probe/cyclone catch. Interestingly, even though calcium was a major component in the probe/cyclone catch, neither it nor magnesium was found in the filter catch. The reasons for this difference are not known at this time.

No evidence was found for the presence of acid in these materials. It is possible that any free oxide present in the sample reacts with the HCl or SO_3 to form a salt. To the extent that this happens, filter weight would be artificially raised, but although not strictly, definitive, the data from this program suggests that filter weight gain via this mechanism is not a serious problem. Details on the qualitative and quantitative composition of the probe/cyclone and filter catches are provided in Appendices E and F. Studies made directly on the filter catch using scanning electron microscopy are described in Appendix H.

TABLE 7

Distribution of Incinerator Particulate Emissions Using EPA Sampling Train

(%)

	Percent Found With Two Types of Incinerators			
	Continuous Grate		Batch	
Collection Device	Range	Ave.	Range	Ave.
Nozzle, Probe, and Cyclone	19-33	23	10-13	11
Filter	49-75	62	70-82	76
Combined Total	74-95	85	83-93	87
Impingers		15		13

TABLE 8

Proportion of Particulate Caught in the Probe Plus Cyclone and Probe Plus Cyclone Plus Filter as Function of Season and Incinerator Type

Sample Code*	Date Sampled	Percent of Catch					
		Probe/Cyclone	Ave.	Filter	Ave.	Probe/Cyclone/Filter	Ave.
NI- 1	4/8/71	20	19	61	67	81	86
2	4/14	16		67		83	
3	4/15	15		65		80	
4	4/15	18		71		89	
5	4/20	26		75		95	
9	4/22	21		65		86	
10	4/22	17		70		87	
13,13A	5/4	24	19	59	60	83	79
22,23,24	5/18	18		55		74	
25,26,27	5/19	16		64		80	
77	10/14	31	33	52	55	83	88
78	10/14	31		58		89	
79	10/14	41		49		90	
80	10/14	28		62		90	
BI-73	9/16	13	11	70	76	83	87
74	9/15	11		82		93	
75	9/16	11		75		86	
76	9/16	10		79		89	

*NI represents continuous grate incinerator.
BI represents batch incinerator.

TABLE 9

Composition of Filter and Probe/Cyclone Catch+

Component	Relative Amounts (%)*			
	Probe/Cyclone		Filter	
Hot Water Solubles		24-60		75
Cations		40-55		40
Anions		24-50		60
Sulfate	10-40		25	
Chloride	5-15		25	
Other$^{\Delta}$ (oxides, silicates, etc.)	~10		10	
Total		25-50		60

+From a continuous grate incinerator.

*See Table 7 for distribution of total particulate catch between Probe/cyclone.

ΔEstimated.

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4.2. CHARACTER OF THE IMPINGER CATCH

As shown in Table 7, the impinger catch amounted to less than 15% of the total particulate catch. Moreover, very little mineral particulate or organic matter was found to be present in the organic extract of the impinger catch. The composition of the impinger catch by the original EPA "dry down" procedure is shown in Table 10 where "dry down" refers to equilibration with Drierite. In comparison, the composition of the impinger catch on an "as received" basis is shown in Table 11. (Water, which is actually most of the sample, is not included in this breakdown.) It can be seen that a large portion of the particulate catch is mineral acid (90-95%). (See Appendices E and F for complete details.)

A more detailed breakdown of the impinger catch is given in Table 12. Recognizing that the impinger catch is only 15% of the total particulate, this means that the non-mineral acid content of the impinger catch is less than 2% of the total material caught in the sampling train--a relatively insignificant sum. Thus, the impinger should not be viewed as a device for collecting solid mineral particulate in this application.

Because the impinger contains only sulfuric and hydrochloric acids, the only chance for false particulate in the impinger comes from the possible oxidation of SO_2 to SO_3 which is then trapped as sulfate. At most, this represents less than 10% of the total particulate catch.

4.3. DISTRIBUTION OF SULFATE AND CHLORIDE BETWEEN THE PROBE/CYCLONE FILTER AND IMPINGERS

The distribution of sulfate and chloride among the various components of the sampling train was found to be different (see Table 13). This difference may be the result of several factors, for example:

- Higher volatility for HCl over SO_3;
- Higher stability of sulfate salts;
- Two different SO_x species present whereas chloride is present only in one oxidation state.

A great deal of work was conducted both in the laboratory and in the field, in an effort to develop an understanding of whether the sulfuric acid in the impingers comes from collection of SO_3 originally present in the stack gas or from oxidation of SO_2 by the train prior to the impingers with subsequent collection of SO_3 in the latter (see Appendix I). Based on calculations of its dew point at 250°F, only 2 ppm SO_3 could be present in the vapor phase. This is equivalent to roughly 13 mg of sulfate. Higher filter box temperature will raise this value but this does not appear to be a sufficient mechanism to explain all of the sulfate in the impingers.

TABLE 10

Composition of Impinger Catch After Evaporation to "Dryness" via EPA Procedures

Component	Amount Found (%)* Continuous Grate	Batch
Sulfuric Acid	46	32
Hydrochloric Acid	2-3	2-3
Ash	2-3	2-3

*Unaccounted components assumed to be mainly water with small amount of organics.

TABLE 11

Composition of Impinger Catch--As Received Basis*

Component	Amount Found (%) Continuous Grate	Batch
Sulfuric Acid	10	8-9
Hydrochloric Acid	86	82
Ash	<1	<1
Organic+	3	8-9

*Not including water, which is bulk of sample.

+Estimated.

TABLE 12

Analysis of Impinger Catch for Continuous Grate Incinerators

Component	Unit^Δ	Sample No.		
		37-3	41-3/43-3	45-3/36-3
Cations	meq.			
H^+(acidity)		15.0	12.3	12.0
Other*		<0.1	<0.1	<0.1
Total (max.)		15.1	12.4	12.1
Anions	meq.			
Sulfate		0.9	1.2	1.0
Chloride		14.8	12.9	12.0
Total		15.7	14.1	13.0
Organic Extractible	mg	<2	<2	<2
Ash @ 850°C	mg	<2	<2	<2

*Other cations were present as follows: (milligrams)

Calcium	0.2	0.5	0.2
Magnesium	0.04	0.07	0.03
Potassium	0.1	0.1	0.1
Sodium	0.3	0.4	0.2
Lead	0.06	0.1	0.2
Zinc	0.05	0.05	0.05
Total	0.8	1.2	0.8

Δmeq = milliequivalents; mg = milligrams.

TABLE 13

Distribution of Chloride and Sulfate in Sampling Train

Sample (NI-)	Distribution of Sulfate (%)				Distribution of Chloride (%)*			
	Probe/Cyclone	Filter	Impinger	Total Weight Found (mg)	Probe/Cyclone	Filter	Impinger	Total Weight Found (mg)
77	28	40	32	70	9	32	59	80
78	16	42	42	103	(8)	--	(208)	220
79	28	34	38	93	11	29	60	105
80	28	26	46	61	(12)	--	(140)	150
Average	25	35	45	82	10	30	60	

*Values in parenthesis are weights in milligrams on a 1.0 m^3 sample basis.

4.4. PROCEDURES FOR MEASUREMENT OF THE PARTICULATE CATCH

The EPA procedure calls for drying of the filter over Drierite before weighing to determine weight gain and thus filter catch. In reality, this approach is a mutual equilibration of water vapor between the filter catch and calcium sulfate (Drierite). If the filter contains materials whose hydrates are more stable than calcium sulfate, the residual water in the Drierite will transfer to the filter. If the reverse is true, the filter catch will give up its water and become "dry."

To demonstrate this problem, we took three samples of impinger water residue representing different total weights and dried them first in a desiccator containing Drierite (calcium sulfate), and then one containing saturated calcium chloride solution. The results were as follows:

	Weight (mg) in Desiccator Containing*		
Sample Code	Drierite	$CaCl_2(H_2O)$	% Gain
NI-23-3	140(8.7)	193(6.4)	38
NI-24-3	37(3.3)	43(0.7)	19
NI-24A-3	17.5(1.0)	20(0.3)	14

*Values in parenthesis are standard deviation (1σ).

Although not dramatically different at the lower levels of particulate, the data does suggest that depending on the drying conditions, a varying amount of water will be called particulate catch. This factor needs more study.

4.5. RELATION TO PRIOR INFORMATION

Although the information developed under this program does not specifically relate to emission levels for each pollutant, we can conclude that our findings are supportive of what has been found in the literature (see Appendix A).

APPENDIX A. COMPOSITION OF INCINERATOR EFFLUENTS

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APPENDIX A

COMPOSITION OF INCINERATOR EFFLUENTS

I. INTRODUCTION

The chemical composition of incinerator stack emissions is principally dependent upon incinerator design and operating conditions, the particular anti-pollution control devices that are employed and refuse composition. The emissions exhibit continual variations in chemistry as a result of moment-to-moment variations in refuse composition and combustion efficiency; furthermore, seasonal variations occur that are mainly due to the influence of yard wastes on average refuse composition.

In addition to variations due to the "incineration" factors given above, chemical measurements are greatly affected by the particular sampling and analysis methods that are employed. As a result, the values for incinerator emissions that are reported in the literature cover a wide range.

This appendix will present a summary of what is known of the composition of incinerator effluents (Section B) as determined by a comprehensive search of the literature. Section C presents annotated biographies of the pertinent literature for each pollutant. Much of the summary data presented herein has appeared in a three volume report to the Environmental Protection Agency (EPA) under contract CPA 22-69-23 by Arthur D. Little, Inc., entitled, "Systems Study of Air Pollution from Municipal Incineration." Sections of that report which are particularly pertinent to emission chemistries are, "The Nature and Causes of Incinerator Air Pollution," Volume I, Sections B through I, and "Incinerator Emissions Data," Volume II, Appendix J. In addition to the above, reference sources have included the open literature, an APTIC (Air Pollution Technical Information Center) literature search based upon the title, "Incineration - Measurement Methods and Combustion Products (Particulates and Particulate Sampling)," and reports based on various studies sponsored by the Office of Air Programs and the Office of Solid Waste Management Programs, EPA.

The following introductory comments serve to preface the discussion of effluent compositions.

- The pertinent literature is mostly from the last decade. Of the 40 references cited herein, 23 are from the period 1966-1970, 12 are from 1960-1965 and 5 are from 1951-1959.
- Many of the reported emissions data are presented with very little discussion of incinerator design, operating parameters, or sampling and analysis procedure. It is difficult to determine the reliability of data in these cases.
- Emissions data for some municipal incinerators have been reported as long as 15 to 20 years ago, with no follow-up studies. These data may be questionable due to the development of more reliable sampling and analysis methodology.

- Very few studies have been performed in a systematic way, that is, with control of refuse composition and incinerator operating parameters. Most such studies have been carried out on low capacity experimental incinerators for obvious reasons.

- Calculated emissions from estimated refuse compositions and combustion parameters are of questionable value due to the large number of variable parameters involved.

- Comparisons of reported data are often difficult or impossible due to the lack of convention in units of conversion. Various units used in the literature for reporting emissions include:

  lbs/ton of refuse
  lb/1000 lb flue gas corrected to 50% excess air
  lb/1000 lb flue gas corrected to 12% CO_2
  grains/standard cubic foot (60°F, 1 atm) at 50% excess air
  grains/standard cubic foot (60°F, 1 atm) at 12% CO_2
  grains/standard cubic foot (60°F, 1 atm) at stack conditions
  grains/cubic meter at NTP (32°F, 1 atm) and 7% CO_2

  The conversion of units depends on refuse composition and incinerator operating parameters, i.e., stack gas flow rate, percent excess air, refuse charging rate, etc. Direct conversion of units is therefore precluded. A set of conversion factors based on representative combustion conditions and typical refuse has been presented by Niessen (Ref. A-1); these factors are given in Table A-1. Summary data reported in this Appendix are presented in terms of pounds per ton of refuse.

The following sections present specific discussions of particulate and gaseous emissions. The solids, which are generally collected in a cyclone or on a filter, are composed of incombustible (mineral) and combustible fractions. The impingers, which collect the condensates, also include fine organic and inorganic particulates which are not previously trapped by a filter. The impinger may also include chemical species which are the product of gas reactions with the impinger solutions.

The gaseous emissions include oxidation products of combustion as well as reaction products of elements released from the refuse, such as hydrogen chloride.

II. SUMMARY OF EMISSIONS

A. Particulates

Particulate has been defined by EPA as "all solids and condensible materials other than uncombined water which are liquid at standard conditions of one atmosphere and 70°F. Particulate matter has almost always been

Table A-1

Conversion Factors for Particulate Incinerator Emissions

	Lbs/Ton Refuse (As Received)	Lbs/1000 Lbs Flue Gas at 50% Excess Air	Lbs/1000 Lbs Flue Gas At 12% CO_2	Grains/SCF at 50% Excess Air	Grains/SCF at 12% CO_2	Grams/Nm^3 At NTP 7% CO_2
Lbs/Ton Refuse (As Received)	1	0.089	0.10	0.047	0.053	0.067
Lbs/1000 lbs Flue Gas at 50% Excess Air	11.27	1	1.12	0.52	0.585	0.74
Lbs/1000 lbs Flue Gas at 12% CO_2	10.0	0.89	1	0.46	0.52	0.66
Grains/SCF at 50% Excess Air	21.31	1.93	2.16	1	1.12	1.42
Grains/SCF at 12% CO_2	18.85	1.61	1.82	0.89	1	1.26
Grams/Nm^3 at NTP, 7% CO_2	15.0	1.36	1.53	0.704	0.79	1

equated to what is collected as particulate at stack conditions rather than what is present in the effluent from the stack. Until recently, it has been taken that, in the EPA train solid particulate was collected by a heated cyclone and/or filter; the materials found in the impingers (and therefore frequently referred to as the impinger catch) is generally referred to as the "condensibles." These may be fine inorganic particulates carried through the filter or organic matter that is trapped in the impinger. In addition, some chemical interactions may occur in the impinger between gaseous species which normally would not condense and the impinger solution.

1. Solid Particulate

The incombustible fraction of the solid particulate that is entrained in the stack gases by the combustion air or combustion products is composed mainly of mineral matter that was present in the waste. Volitalization and condensation of metals also contributes to the mineral particulates but, for mixed wastes, this usually contributes only a small fraction of the total mineral particulate loading. The combustible fraction consists of char (blackbirds) entrained from the grate, "black smoke" (soot) produced by the thermal cracking of pyrolysis products before these have been mixed with sufficient oxygen to complete their combustion, and "white smoke" produced by the condensation of pyrolysis gases.

• Mineral Particulate

An appreciation for the factors that determine particulate emission and for their relative importance may be gained by considering the two mechanisms mainly responsible for the emissions:

- The mechanical entrainment of particles from the burning refuse bed;
- The volatilization of metallic salts or oxides.

The first of these mechanisms is favored by refuse with a high percentage of small particle size, low density ash; by residue or residue geometry favoring entrainment (plates); by high underfire air velocities; and by other factors that induce a high gas velocity through the bed. The second mechanism is favored by a high concentration of metals that form low melting point oxides and by high temperatures within the bed.

• Mechanical Entrainment

Ash particles may be entrained when the velocity of the gases through the fuel bed exceeds the terminal velocity of the particles. Undergrate air velocities typically vary from a minimum of 10SCFM/sq. ft. of grate area to 100 SCFM/sq. ft. Based on the terminal velocity of ash particles it is therefore expected that particles up to 70 μm (equivalent diameter) will be entrained at the lowest velocities and up to 400 μ at the highest. These data are shown in Figure A-1.

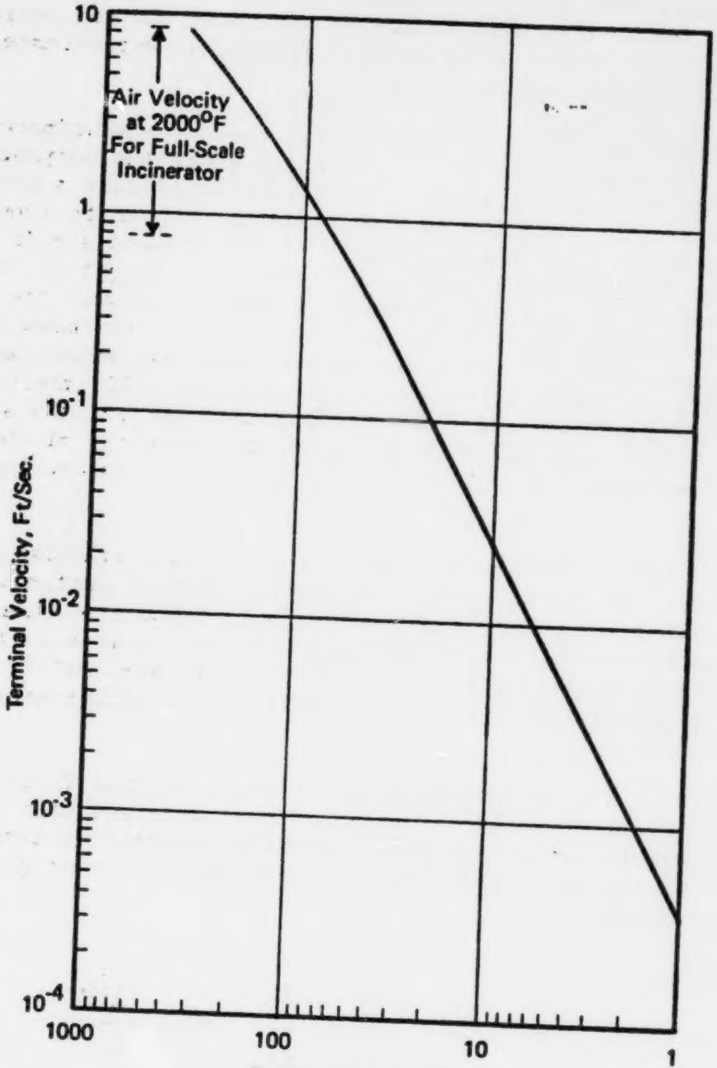

FIGURE A-1

Particle Fluidization Velocities (Terminal Velocities)

Overall findings show that the ash content of the refuse is a major factor in determining emission rates, and that the percentage of the ash carried over ranges mostly between 10 and 20% of the total, corresponding to 15 pounds/ton of refuse on the average. The actual percentage carried over for a particular incinerator will, of course, depend on other factors such as underfire air rate. On the average, a two-fold reduction in air velocity will produce an approximately 30 percent reduction in emission rate.

Entrainment of mineral particulate, however, cannot be eliminated completely by the elimination of underfire air since the buoyancy of the combustion gases will induce an air flow that will produce a minimum particulate emission. From dimensional analysis, it can be shown that for a buoyancy-driven flow the velocity V of the induced air is proportional to $\sqrt{L\Delta\rho/\rho g}$ where L is a characteristic length of the combustion chamber, $\Delta\rho$ is the difference in density between the colder entrained gases and the hot combustion products, ρ is the mean density of the combustion products, and g is the gravitational acceleration. Entrainment of particulate by buoyancy-driven flows will, therefore, increase with furnace size and flame temperature. An additional factor that enhances particulate emission is agitation (stoking) of the burning waste but the magnitude of this factor has not been quantitatively established.

Emissions to the atmosphere depend greatly upon the particular anti-pollution control equipment that is employed. Mineral particulates are mostly composed of SiO_2, CaO, Al_2O_3 and Fe_2O_3. These are often present as complex compounds, which also may contain appreciable amounts of sodium and potassium. Variation in flyash chemistries, particularly for iron and aluminum compounds, are largely due to differences in the refuse composition.

Particle size distribution measurements of stack emitted flyash show that over 90 percent by weight of the particles are less than 250 μm and about 10 percent are sub-micron. Recently reported studies of particle size distribution give the following values for weight percent smaller than indicated size.

	Size (μm)						
	5	10	15	20	30	45	150
Ref. A-2	15	25	--	40	--	60	--
Ref. A-3	37	64	75	81	87	--	--
Ref. A-4	6	20	--	47	69	89	--
Ref. A-5	20	42	52	58	70	77	95
Ref. A-6	20	29	44	--	57	62	--
Ref. A-7	12	18	39	42	44	60	95
Average	18	33	52	53	65	70	95

These data are compared to particle size distributions measured for three typical U. S. incinerators, European practice and both coal- and oil-fired boilers in Figure A-2. It is of interest to mention that emissions of 3 to 5 lbs particulate/ton of refuse correspond to about 10^{15} individual particles, half of which are less than 0.05 μm and 95% of which are less than 0.1 μm in size.

The flyash particulate can have an important influence on other chemical emissions. Since a great many particles are in the sub-micron particle size range, they could serve as condensation nuclei for many vapor species. In addition, the relatively high alkaline earth contents of flyash and the high moisture content in flue gases allows a certain level of SO_2 and SO_3 absorption, resulting in the formation of alkaline earth sulfates. Finally, the large surface area of the particulates is favorable for adsorbing certain gas species. These factors tend to influence the total weight of particulate and should be taken into account when performing a materials mass balance.

• Volatilization of Metallic Salts

The temperature within a burning refuse bed can reach 2500-3000°F. At these temperatures, a number of metal salts (particularly those of the alkali metals) will vaporize or sublime. Therefore, it would appear that although volatilization of salts may be occurring in localized hot spots within the burning bed, the low concentration of these salts in refuse, the low frequency and/or intensity of the hot spots, condensation of the vapors within cooler regions of the bed, or other considerations prevent or attenuate emission. The contribution of metallic salt volatilization to the total furnace particulate emission rate thus appears to be small in municipal-scale incinerators.

• Combustible Particulate

Combustible particulate consists of char (blackbirds) entrained from the grate, soot (black smoke) produced by the thermal cracking of pyrolysis products before these have been mixed with sufficient oxygen to complete their combustion, and an aerosol (white smoke) produced by the quenching of pyrolysis products before they have reacted. All three are highly visible and have a nuisance value in excess of their contribution to the total particulate emission rate.

Char formed from paper or sheets of other carbonizable material has a high surface-to-volume ratio, and is, therefore, entrained at relatively low velocities, in amounts that depend on the make-up and degree of agitation of the refuse bed. Inert material in the bed has a beneficial effect of keeping elements of char from being entrained. No quantitative estimate of the emission rate of charred waste components is available, but it is believed to be a small fraction of the total particulate emission.

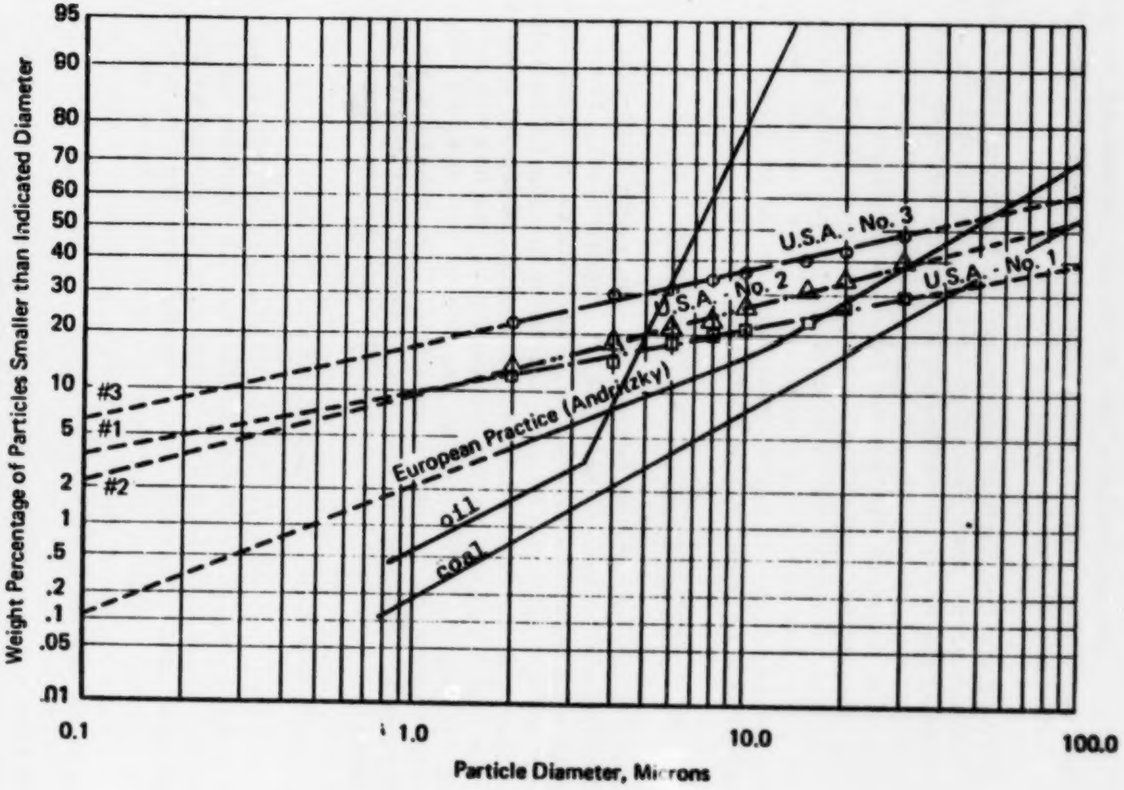

FIGURE A-2

Particle Size Distributions of Furnace Effluents

Sources: European: Andritzky, M., Brennstoff-Warme-Kraft 19(9), 436(1967); U.S.A: Walker, A.B., and Schmitz, F.W., Proc. 1966 ASME Nat'l. Incin. Conf., pp 64-73.

The second source of combustible material, soot, is usually the most significant one. Soot particles, once formed, are relatively difficult to burn, and as a consequence of their characteristically small dimensions, are difficult to collect. The best form of control of black smoke is, therefore, the prevention of soot formation. This can be achieved by the rapid mixing of the pyrolysis gases with sufficient air to complete their combustion since it has been shown that with perfect mixing little soot is formed even under fuel-rich conditions. For example, Wright (A-8) has found that for a wide range of hydrocarbons burned in a well-stirred reactor, the atomic ratio of oxygen to carbon at which soot was first detected ranged from 1.35 to 1.81, well below the stoichiometric ratio of 2.00. The practical significance of these results is that soot formation may be prevented by the proper design and placement of overfire air or steam jets.

The mechanism of soot formation is so complex, however, that the amounts of combustible particulate that leave a furnace chamber cannot be reliably estimated. The amounts of soot formed are a measure of the poor mixing conditions in a chamber and are expected to be greatest when a furnace is overcharged or when a waste having a high fraction of volatile carbon (total minus fixed carbon) is burned. Under normal operating conditions, the average combustible fraction of the particulates leaving combustion chambers of municipal incinerators is found to be about 15 percent (A-1); but because soot forms as sub-micron particles, it is difficult to collect and the fraction of combustible in the particulates leaving air pollution control devices can be considerably higher. Contemporary, continuous-feed municipal incinerators, for example, emit an average of 3.9 lbs combustible/ton refuse, a figure which corresponds to about 20 percent of the total particulate.

The third type of combustible particulate emission is the aerosol of unreacted hydrocarbons which is formed when the pyrolysis products evolved on the grate are cooled and condense before mixing with hot furnace gases. The white smokes that are produced usually consist of fine particles (<2μm) which are difficult to collect. Such emission, however, is relatively infrequent and can be eliminated by either afterburning or the adjustment of the air flow to a furnace to provide better overbed mixing.

2. Condensible Particulate (Impinger Catch)

The impinger catch includes vapor condensates and fine sub-micron ash particles which have passed the primary particle collector (cyclone or filter). Collected material that would have remained gaseous had it been directly admitted to the atmosphere but instead has condensed in the sampling apparatus clearly should not be included as part of the condensible particulate catch.

Studies of condensible particulates have been quite limited. The particulate caught after the filter corresponds to about 30 percent of the total. Roughly two-thirds of this appears as inorganic (by definition of the extraction treatment) and is thought to represent flyash "fines" which have penetrated the filter. The other third, or about 10 percent of the total particulate, is organic in nature. There has been an insufficient amount of work reported in the literature to indicate the mechanisms by which these materials are captured by the impingers. Further it is not clear whether these materials enter the impingers as solids or condensible vapors or if any portion is formed by combustion gas interaction with the impinger liquids.

B. Gaseous Emissions

The major flue gas components that are routinely reported in measurements of incinerator emissions include oxygen, nitrogen, water and CO_2. Other gas species, present in relatively small quantities, constitute the major gaseous pollutants. These gases, which are formed directly by the combustion process or indirectly by chemical interactions within the gas stream, include carbon monoxide, sulfur oxides, nitrogen oxides, ammonia, inorganic acids (HCl, HF, etc.) and various organics including acids, aldehydes, esters, hydrocarbons, polynuclear hydrocarbons and others (alcohol, ketones, mercaptains, organometallics, nitriles, amides, sulfones, etc.) The organic species are identified and quantitated by combined methods of infrared spectrometry, gas chromatography and mass spectrometry.

The major gaseous species within incinerator emissions have composition ranges of 10-13% O_2, 3-5% CO_2, and 10-30% H_2O, or on a dry basis, 13-15% O_2 and 4-8% CO_2 with the balance being N_2. Continuous monitoring of these gases, either by Orsat analysis or by continuous gas sampling, provides the necessary data to convert emissions to a common basis, i.e., 50% excess air (STP) or 12% CO_2 (STP).

1. Carbon Oxides

Carbon monoxide is the most significant pollutant (on a weight basis) emitted from municipal incinerators. Although it is reported that the level of CO can be reduced by increasing the amount of excess air, the resulting increased stream velocities of the exit gases cause entrainment of an additional fraction of the ash residue, leading to an increase in flyash emissions. The reported levels of CO emissions vary considerably, ranging from 0.3 to over 200 pounds/ton of refuse burned.

Carbon monoxide is generally measured by Orsat analysis. This method has a detectibility limit of 0.1 volume percent which, for typical incineration conditions of 200% excess air and stack gas temperature of 500°F, corresponds to 9 pounds CO/ton of refuse. The very poor sensitivity of Orsat analysis leads to a wide range of reported emission levels.

An additional difficulty is encountered in converting measured CO volumes to lbs/ton of refuse. Rigorous conversion requires knowledge of the stack gas volume per unit time and rate of refuse burning, parameters which are seldom given. Approximate conversions can be made which are based upon the weight of dry air required to burn a pound of typical refuse or upon a carbon balance. The latter is computed on the basis of 500 lbs carbon/ton of refuse, yielding:

$$1.17 \times 10^3 \quad \frac{v/o\ CO}{v/o\ CO + v/o\ CO_2} = \text{lbs CO/ton of refuse.}$$

This computation yields a maximum level of CO, for it assumes that all carbon in the refuse is converted to the oxide.

Stack gas analyses from 16 incinerators representing 122 individual measurements average 23.8 lbs CO/ton of refuse with a standard deviation of 34.2 lbs/ton. A more comprehensive study of 33 units and 302 individual data points carried out by Niessen (A-1) yields an average of 33.2 lbs CO/ton of refuse with a standard deviation of 34.1 lbs/ton. The estimated average emission factor for U. S. incinerators was 34.8 lbs/ton.

The values given above represent maximum CO levels, as they were calculated according to a carbon balance. Kaiser (A-9) suggests that 25% of the carbon (i.e., 125 lbs/ton of refuse) is carried over to the ash residue as unburned char. For this case, the reported CO average emission would be 17.9 lbs/ton of refuse or, according to Niessen 26.1 lbs/ton of refuse.

2. Sulfur Oxides

The level of SO_2 emissions is reported to be directly related to the sulfur content of refuse, which is given in several reports as 0.1% by weight. This concentration would provide a maximum SO_2 level of 4 pounds/ton of refuse. Various reports of the SO_2 content of incinerator emissions range from 0.7 to 3.9 pounds/ton of refuse, with an average of 2.2 pounds/ton of refuse. The remaining sulfur is believed to be tied up as sulfate in the ash residue and flyash and as condensed H_2SO_4. Niessen (A-1) takes exception to the above and concluded that 95% of the gaseous sulfur is emitted as SO_2; he concludes that reports of high levels of SO_3 are the result of sampling and analysis errors.

3. Nitrogen Oxides

The content of nitrogen oxides is small since the temperature required for their copious production (> 2000°F) are generally not reached during incineration. Typical levels are 90 ppm (3.1 lbs/ton of refuse) at temperatures of 2000°F. The reported range of nitrogen oxide emissions is 0.3 to 5.7 lbs/ton of refuse, with an average of 2.1 lbs/ton of refuse. In contrast to the above, a study of seasonal variation in incinerator emissions in the New York City area (A-10) yielded average values of about 0.05 lbs/ton of refuse for both NO and NO_2.

4. Hydrocarbons

Hydrocarbons represent a relatively small fraction of the total emitted pollutants. The combustion of hydrocarbons is a two-step process: rapid oxidation to CO followed by slow oxidation to CO_2. As a result, hydrocarbon emissions can often be correlated with CO emissions. Literature data on hydrocarbon emissions range from 0.3 to 2.7 lbs/ton of refuse.

5. Specific Organics

Very limited data are available for the levels of specific organic classes present in municipal incinerator effluents. Concentrations reported are generally in the range of 1 ppm or less, corresponding to approximately 0.01 lbs/ton of refuse. Polynuclear hydrocarbons are reported at levels of 5×10^{-5} to 10^{-3} lbs/ton or refuse. Numerous organic compounds, all present in very small quantities, have been identified as being present in incinerator emissions.

6. Inorganic Acids

HCl emissions are of major concern. Although HCl emissions in the past were generally low (less than 1 lb/ton of refuse), the increased usage of chlorinated plastics for disposable packaging materials suggests a greatly increased growth in HCl emissions in the future. Anticipated growth patterns developed by Niessen (A-1) indicate expected average emissions (in pounds per ton of refuse) of 1.5 in 1970, 2.2 in 1975, 2.7 in 1980, 4.4 in 1990 and 5.4 in 2000.

HF is also probably present in incinerator emissions, most of which results from combustion of fluorinated hydrocarbons such as "Teflon." Limited studies indicate HF levels of 0.002 to 0.2 lbs/ton of refuse.

It is anticipated that properly designed wet scrubber APC systems may remove up to 99% of the HCl and HF, thus reducing the pollution hazard.

7. Volatile Metals

Some metals, particularly Zn, Cd and Pb are volatile or have oxides that are volatile at incineration temperatures. In general, very small particles are formed. Little quantitative data are available for metal emissions. Based upon the lead content of refuse, emissions are about 0.03 lbs of lead/ton of refuse. Selenium emissions are of particular interest due to its toxicity. The one published measurement of Se reports 0.002 lbs/ton of refuse.

C. Summary

In summary, the studies of municipal incinerator emissions are limited in number as well as in scope. The reported results vary widely depending upon refuse composition, incinerator type and operating conditions, employment of various types of APC devices, and sampling and analysis procedures. Although there have been about half a dozen comprehensive studies of incinerator emissions over the past fifteen years, there is no specific agreement in the collected data. A description of the composition of incinerator effluents is therefore rather vague. Based upon the results of the literature survey, the following estimates are made for incinerator emissions. The results obtained by Niessen (A-1) in a recent study are presented for comparison.

Component	Pounds/Ton of Refuse		
	Range	Average	Ref.A-1
Solid Particulate	1.9-23.0	7.2	13.6
CO	0-202	23.8	34.8
SO_x (as SO_2)	0.7-3.9	2.2	3.9
NO_x (as NO_2)	0.05-5.7	2.1	2.6
Hydrocarbons	0.3-2.7	1.0	2.7
Polynuclear Hydrocarbons	$5x10^{-5}$	$5x10^{-5}$	$3.2x10^{-3}$
HCl	--	--	0.8
HF	--	--	$2x10^{-2}$
Pb	--	--	$3x10^{-2}$

III. ANNOTATED BIBLIOGRAPHY OF INCINERATOR EMISSIONS

Annotations to literature references describing the chemistry of incinerator emissions are presented chronologically for the following categories: particulates, carbon oxides, sulfur oxides, nitrogen oxides, hydrocarbons, specific organics (including acids, aldehydes and polynuclear hydrocarbons), inorganic acids and volatile metals. These annotations are sufficiently complete so as to provide a preliminary information source to the literature for any of the above chemical categories. The reader is directed to the cited references for more specific discussions. A reference listing is presented at the end of this section.

A summary sheet is presented in Table A-1 which specifies the availability of literature data for each of the chemical specie categories in terms of effluent chemistry, sampling and analysis procedures, incinerator operating practice, chemical interactions and so forth. The references cited in this table are ranked according to the value of the data reported.

TABLE A-2

Summary of Abstracted Incinerator Emissions Data

References*

Effluent Chemistry	Particulate	Carbon Oxides	Sulfur Oxides	Nitrogen Oxides	Hydrocarbons	Specific Organics	Inorganic Acids	Volatile Metals
a. Gaseous		9,11,16,(17), (29)	14,34,38, (31),(36)	10,20,22,25, 37,(30)	22,23,24,25,29, (2)	17,18,20,22,30, (2)	34	27
b. Particulate	4,15,16,22,23, 24,27,(2),(13), (20),(26)							
c. Fly Ash	4,11,18,5,6, 7,9,14,27							
d. Particle Size Distribution	2,3,4,5,6,7,15							
f. Influence from APC device	2,13,15	11,16						
Sampling Procedure	11,12,18,20,21, 23.25	18,9,11,17, 20,26	18,20	18,17,20,23, 25,26		18,22		
Analysis Procedure	18,23,25	9,11,20,22, 23,24,25,28	18,20,33	18,20,23,25	22,23,25,39	18,20,22,40		
Influence by Incinerator Operating Parameters	22,23,24,25	18,23,24,25	(32)	22, 25, 23,24	24,25			
Chemical Interations in Effluent	14,(25)	9	14					
Chemical Correlation	12	9,18,20,23, 24,25		25				
General	17,(19)		(35)	20,30,(13)				

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*References that are underlined are thorough and complete; references in parenthesis have sketchy information which is difficult to evaluate.

A. Particulates

1. Bibliography

Reference A-11 (1970)

A comprehensive evaluation of the performance of seven incinerators is presented which has determined: (1) the quality and quantity of solid waste processed, residue, and gas borne particulate emissions, (2) the quality of the flyash collected and the waste water produced, and (3) the economics involved in incineration. The sampling procedure employs the PHS sampling train and the resulting chemical analyses are discussed in detail. Particulate emissions range from 8.6 to 20.4 pounds per ton of refuse, with an average of 12.5. In all cases, these emissions exceeded the most lenient air pollution grain-loading emission standards.

The particulates caught after the filter average 30% of the total particulate catch including (1) residue left after evaporation of the acetone used to rinse the sampling train from after the filter to before the impinger that contains the silica gel, (2) residue left after evaporation of the chloroform and ether used to extract organic materials from the impinger water wash, and (3) residue after evaporation of the impinger water wash. The residues from the acetone wash and from the chloroform-ether extracts average 30 percent of the material caught after the filter; the inorganic residue from the impinger water wash is 70 percent. Approximately 0.05 percent of the residue is metal. The most abundant metallic species were Ca (400 ppm), Zn (100 ppm), Al (25 ppm), Mg (13 ppm) and Fe (6 ppm).

Several impinger residue samples were combined into two test lots for wet-chemical analysis for inorganics and instrumental analysis for organics. Approximately 28 and 43 percent, respectively, of these residues were acetone soluble. Sulfates were present in approximately 32 and 20 percent, respectively. The acetone extract of both samples showed carbonyl and aromatic bands in the infrared (presumably derived from polynuclear compounds). No hydroxyl or aliphatic bands were noted.

The reported analyses indicate that perhaps some of the material caught after the filter should be reported as particulates and some should not. The organics and metals would clearly be classified as particulates. The chlorides, sulfates, and phosphates, however, may be formed by gases reacting with cations to form particulates while in close contact in the impinger water. If so, they probably would not react if emitted to the atmosphere and would not fall within the category of particulates.

Further work is needed on identifying composition of impinger water residues and their origin since the cited work was "primarily a screening."

Reference A-12 (1970)

This paper describes a laboratory scale program to evaluate source-sampling equipment used to measure particulate emissions from incinerators. Tests involving simultaneous sampling using the IIA T-6 train and the PHS train exhibited results which varied appreciably for the two systems.

Reference A-13 (1968)

Typical estimates of particulate emissions are 1.6 grains/SCF corrected to 50 percent excess air. Current recommended standards range from 0.35 to 0.05 grains/SCF (50 percent excess air) which requires from 82 to 97 percent removal by APC devices. A comparison of the effectiveness of various APC systems for particulate removal is discussed.

Reference A-14 (1968)

Although the article is principally concerned with calculating a sulfur mass balance between refuse and incinerator emissions, data are given for typical fly ash compositions collected in the hot flue gases, the dust zone and in the stack. The SO_3 content of the fly ash was found to increase proportionate to combined alkaline earth contents. The author concludes that about 25 percent of the sulfur introduced in refuse is tied up in the fly ash as sulfate.

The table below presents typical chemical analyses of fly ash sampled in the hot flue gases, in the dust collection zones, and in the stacks.

Chemical Analysis

	A	B	C
Organic	31	4	21
Inorganic	69	96	79
Inorganic Fraction			
SiO_2	47.2	48.7	36.5
Al_2O	10.2	23.4	25.9
TiO_2		1.1	0.7
Fe_2O_2	15.6	6.5	7.1
CaO	18.4	9.2	8.9
MgO	2.9	2.3	2.8
$Na_2O + K_2O$	4.5	5.8	10.5
SO_2	1.2	3.0	7.6
	100.0	100.0	100.0

A. Suspended in hot flue gases.
B. Dust collection zones.
C. Collected in stack.

Reference A-15 (1968)

This paper reviews and discusses the incinerator emissions problem, methods of particulate emissions control and their relative cost. Incinerator dust size measurements, determined in the BAHCO centrifugal classifier using the methods and procedures of ASME Performance Test Code No. 28, indicate that about 35 percent of the average dust leaving the furnace is below ten microns in size. Furance dust emissions vary from less than 10 pound/ to 60 pound/ton of refuse. High-performance turbulent incinerators emit about 35 pounds/ton.

Various types of APC devices are described. Multi-cyclones are extremely efficient for large particles, but performance drops off rapidly for dust sizes smaller than 20 microns.

Reference A-2 (1968)

A compilation of air pollutant emission factors is presented, including fly ash particle size distributions, collection efficiencies of various APC devices and the composition of gaseous emissions. A sizable bibliography is included.

Municipal incinerators are quoted as emitting 17 pounds particulate/ton of refuse with the following size distributions.

Size Range (μm)	Weight Percent
less than 5	15
5-10	10
10-20	15
20-40	20
greater than 44	40

Reference A-16 (1967)

The maximum stack emission rates measured on the North Hemstead, New York, 3-unit incinerator system averaged 2.43 pounds particulate/ton of refuse for 8 tests carried out over 5 days. Other New York area incinerators exhibit particulate emissions of 2.3 to 30 pounds/ton of refuse for 10 incinerators cited.

Reference A-17 (1967)

This paper describes the initiation of incinerator testing in the New York City area to (1) evaluate seasonal variations in refuse and stack emissions, (2) identify and quantify specific inorganic and organic emissions and (3) to compare emissions from four different types of incinerators. The preparation of a sampling train and initial test results are described.

Reference A-19 (1967)

A specific procedure for incinerator stack sampling is presented, using experience in the Los Angeles area as a guide. Sampling and analysis methods for specific pollutants are reviewed in detail. Spectrographic analysis of two samples of solid particulate yields the following results:

Particulate - Weight Percent

Component	From Multiple Chamber Incinerators	
Aluminum	1.2	0.34
Boron	0.32	0.32
Calcium	0.92	0.50
Chromium	0.14	3.7
Cobalt	0.0015	0.026
Copper	0.13	0.015
Iron	1.8	19.5
Lead	0.33	0.11
Magnesium	1.3	1.0
Manganese	0.18	0.11
Molybdenum	0.0093	0.003
Nickel	0.16	2.8
Potassium	Trace	--
Silicon	12.0	2.7
Silver	0.016	--
Sodium	Trace	--
Tin	0.031	0.020
Titanium	0.022	0.0099
Vanadium	0.0012	0.014
Zinc	3.2	0.51
Zirconium	0.010	

Reference A-4 (1966)

A comprehensive series of tests were carried out on a new municipal incinerator to establish performance data. Total particulate emissions were in the range of 6 to 12 pounds/ton of refuse, with an average for 17 tests of 7.8 pounds/ton of refuse. Spectrographic and chemical analysis results and particle size distributions of the fly ash are as follows:

Spectrographic Analyses
Elements Reported in Percent Ashed Material

Element	Dust Test Run No. 6			Dust Test Run No. 8
	Stack Effluent	Collector Catch	Residue	Stack Effluent
Silicon	5+	10+	10+	5+
Manganese	.1-1.0	.1-1.0	.1-1.0	.1-1.0
Chromium	.1-1.0	.01-.1	.01-.1	.1-1.0
Nickel	1-10	.001-.01	.001-.01	10+
Copper	.1-1.0	.01-.1	.01-.1	.1-1.0
Vanadium	.001-.01	.01-.1	.01-.1	.001-.01
Iron	.5-5.0	.5-5.0	1-10	.1-1.0
Tin	.05-.5	.-5-.5	.1-1.0	.001-.01
Aluminum	1-10	1-10	1-10	.1-1.0
Zinc	1-10	1-10	.1-1.0	.1-1.0
Magnesium	1-10	1-10	1-10	1-10
Titanium	.5-5.0	.5-5.0	1-10	1-10
Silver	.001-.01	.001-.01	.5-5.0	.5-5.0
Boron	.01-.1	.01-.1	.0001-.001	-.0001
Barium	.1-.1	.1-1.0	.01-.1	.01-.1
Beryllium	.001-.01	.001-.01	.1-1.0	.1-1.0
Calcium	10+	10+	-.001	-.001
Sodium	1-10	.5-5.0	10+	10+
Lead	.01-.1	.1-1.0	.1-1.0	1-10

Wet Chemistry Analyses

pH	8.3	12.3	12.3	7.7
Sulphur	---	.620	.350	---
Phosphorus	1.460	1.760	1.390	1.140
Silicate	---	---	---	5.4
Anions				
Phosphates	.88	---	---	.77
Nitrates	.62	---	---	.64
Sulfates	.50	---	---	2.1
Chlorides	.02	---	---	.22

Particle Size Analysis

Density: 1.85 grams per cubic centimeter

Microns	Percent by Weight Less Than the Stated Size
44	89.2
30	68.7
20	47.2
10	20.5
5	6.0

Reference A-19 (1966)

No chemical or sampling information given. However, this study reports that limiting the excess air to a maximum of 25 to 50 percent minimizes the entrainment of particulates in the exhaust gas.

Reference A-6 (1966)

Total incinerator emissions are given for several Western European incinerators. Representative fly ash compositions and particle size distributions are given below. There is no discussion of sampling or analysis methodology.

Chemical Analysis of Fly Ash
(Percent by Weight)

	Collected Portion	Discharged Portion
Organic	0.5	15.0
Inorganic	99.5	85.0
Silicon as SiO_2	52.4	36.1
Aluminum as Al_2O_3	21.5	25.1
Iron as Fe_2O_3	5.7	7.1
Calcium as CaO	7.8	8.6
Magnesium as MgO	1.8	2.4
Sodium as NA_2O	3.7	6.0
Potassium as K_2O	3.8	5.9
Sulfur as SO_2	3.3	8.9
	100.2	100.0

Size Distribution of Stack Dust Emission

Size Microns	Distribution Percent	Cumulative Percent
+840	0.4	0.4
+250	3.2	3.6
+149	8.4	12.0
+ 74	17.6	30.4
+ 43	5.4	35.8
+ 40	5.3	41.1
+ 28	13.3	54.4
+ 15	14.1	68.5
+ 9	9.6	78.1
+ 4	11.9	90.0
+ 2	6.7	96.7

Reference A-20 (1964)

Test data are presented for flue gas compositions and total particulate emissions for two municipal incinerators. Particulate emissions from the stack correspond to 2.6 lbs/ton of refuse. The benzene soluble fraction of the particulate is less than 1 percent. Sampling and analysis procedures are as follows:

The gas stream is passed through a series of water bubblers kept at 32°F, then a series of freeze-out traps immersed in a dry-ice-alcohol bath held at -98°F, and a high-efficiency glass-fiber filter (MSA type 1106-BH). Isokinetic sampling conditions range from 4-6 SCFM. Total weight of particulates is determined by collecting material from the sampling probe and from the sampling train filter; material filtered from the condensate and liquids used to rinse the train; and material recovered from evaporation of the condensate and water rinses. The measured emissions from several municipal incentors are as follows:

POLLUTANT EMISSION SUMMARY

		Flue-Gas Conditions			Total Particulates	
			CO_2	O_2		
			Dry Basis			
Type of Unit	Sampling Point	H_2O %	%	%	Lbs. per Ton of Refuse	% Benzene Soluble Organics
Municipal 250-Ton/Day Multiple Chamber	Breeching (before settling chamber)	8.8	6.2	13.7	18	0.32
50-Ton/Day	Breeching (before scrubber)	9.1	8.7	11.0	8.1	0.15
	Stack (after scrubber)	12.4	3.7	16.7	2.6	0.96

Reference A-9 (1964)

In a study where measured incinerator stack emissions are compared to calculated emissions based upon refuse composition, the following compositions are given for fly ash (average of five tests)

SO_2	0.1	MgO	9.3
Al_2O_3	6.2	Na_2O	4.3
FeO_3	2.6	K_2O	3.5
CaO	14.8	SO_3	0.1

Reference A-21 (1964)

This program resulted in the construction of a prototype instrument for the analysis of fly ash emitted from municipal incinerators. The instrument was proven both in the laboratory and in the field. The instrument samples a predetermined amount of stack effluent isokinetically, separates the particulate material in a cyclone, collects a representative sample of fly ash on filter paper, and measures the amount of sample by a gravimetric technique using a beta-gauge principle. The entire concept is designed to function on a routine basis and be operated by unskilled personnel.

Reference A-22 (1962)

A sequence of field tests was made on full scale incinerators to determine the relationship between underfire air and particulate emissions in terms of incinerators of different sizes and designs. Findings: There appears to be a critical level of underfire air for large municipal incinerators beyond which particulate emissions do not increase significantly. On the two units tested this change in trend occurred at an underfire airflow between 35 and 40 SCFM/sq. ft. of grate area. The use of 50% overfire and 50% underfire air approaches an ideal distribution causing the maximum burning rate which also keeps the particulate emissions well below the loadings which result when using higher underair percentages. The sampling techniques are the same as those described in Reference A-25. Results are as follows:

Combustion Conditions			Emissions	
Underfire Air - %	Excess Air - %	Temp. Secondary Chamber - %	Before Scrubber	After Scrubber
50 Ton/Day Batch Charge Incinerator				
20	235	1080	0.78*	0.57*
50	110	1500	1.01	0.55
70	100	1500	1.79	0.61
20	215	--	6.8**	4.1**
55	110	--	8.6	4.7
60	100	--	15.5	5.7
250 Ton/Day Continuous Charge Incinerator				
20	190	1750		3.8*
50	180	1790		2.8
80	190	1930		3.3
100	150	1960		4.6

*Pounds Particulate/1000 Pounds Dry Flue Gas (connected to 50% excess air)
**Pounds Particulate (Ton of Refuse Burned).

Reference A-7 (1961)

The composition and particle size distributions of fly ash are given for tests carried out on the Gansevoort Incinerator, New York City, summarized as follows:

Chemical Analysis of Fly Ash Emitted from
Gansevoort Incinerator, New York City

Component	Percent by Weight
Organic	14.5
Inorganic	85.5
Silica as SiO_2	36.0
Iron as Fe_2O_3	10.0
Alumina as Al_2O_3	27.7
Calcium as CaO	8.5
Magnesia as MgO	3.4
Sulfur as SO_3	9.7
Sodium and potassium oxides	4.7
Apparent specific gravity	2.58

Reference A-7 (continued)

Particle Size of Fly Ash Emitted from Gansevoort Incinerator, New York City

Size	Percent by Weight
Plus 120 microns	5.8
Plus 90 microns minus 120 microns	6.5
Plus 60 microns minus 90 microns	17.7
Plus 40 microns minus 60 microns	13.2
Plus 30 microns minus 40 microns	12.5
Plus 20 microns minus 30 microns	1.9
Plus 10 microns minus 15 microns	21.2
Plus 5 microns minus 10 microns	5.8
Minus 5 microns	12.0

Reference A-23 (1960)

This reference is one of a series (Ref. A-23, A-24, A-25) describing the effects of incinerator operating conditions on pollution emissions. The present paper cites the results obtained with a highly volatile fuel component (asphalt saturated felt roofing). Particulate loadings were determined by collecting samples on a seven inch diameter glass fiber filter; samples taken under isokinetic conditions at a representative velocity point in the stack. The experimental multichamber incinerator that was employed is described in detail. Particulate emissions were higher with asphalt roofing material than with cellulose fuel. With the asphalt roofing, minimum discharge was 2.6 lb./ton. With worst conditions of underfire air, excess air and fuel feed rate, particulate emissions were 47.2 lb./ton. With large batch charging added, particulates increased up to 65 lb./ton. Large batch charging with only 50% excess combustions air resulted in up to 84 lb./ton. Cellulose fuel tested discharged from 0.8 lb./ton to 9.0 lb./ton maximum.

To separate solid particulate into noncombustible (or nonvolatile) and combustible (or volatile) components, particulate samples were subjected to a temperature of 550°C for three hours and checked for weight loss. In general, the noncombustible-nonvolatile component of particulate amounted to less than 20% of the total weight. Only one test condition (with 40% noncombustible content) was higher, and this occurred under optimum combustion conditions. Tests made at the 50% excess air level had only 5% noncombustible content.

Results are summarized in the following Table:

Excess Combustion Air	Fuel Feed Rate (lb/hr)	Air Distribution			Particulate		
		Underfire	Overfire	Secondary	Gr/Sc.f	Lb/Ton Fuel	%Ash
50%	150	80%	20%	0	1.31	58.4	5.7
		80%	20%	0	1.94	84.0	3.9
100%	100	10%	83%	0	0.09	5.3	20.2
		22%	77%	0	0.24	14.4	7.9
		60%	40%	0	0.27	15.6	11.7
		90%	10%	0	0.33	19.8	14.2
		15%	85%	0	0.44	19.2	6.7
		60%	40%	0	1.11	65.0	7.0
	150	15%	85%	0	0.04	2.6	38.4
		60%	40%	0	0.23	13.3	12.6
		60%	15%	25%	0.25	14.4	9.4
		15%	85%	0%	0.09	5.9	18.5
		60%	40%	0	0.59	34.0	7.8
		60%	15%	25%	0.02	35.6	4.8
150%	150	12%	68%	20%	0.00	6.3	19.4
		48%	12%	40%	0.28	19.6	9.1
		48%	12%	40%	0.36	27.6	7.4
200%	100	15%	85%	0	0.40	34.4	8.4
		60%	40%	0	0.44	36.4	11.5
		15%	85%	0	0.41	38.0	0.7
		60%	40%	0	0.59	52.8	7.7
	150	10%	90%	0	0.14	11.2	19.1
		15%	85%	0	0.19	14.8	17.2
		40%	60%	0	0.47	41.8	12.7
		40%	10%	50%	0.39	32.4	6.9
		60%	40%	0	0.54	47.2	19.9
		15%	85%	0	0.22	18.6	13.2
		60%	40%	0	0.41	34.0	17.6
300%	100	15%	85%	0	0.42	47.0	9.4
		60%	40%	0	0.64	78.2	11.9

Reference R-24 (1960)

In a continuation of experimental studies of the influence of incinerator parameters on pollution emissions (Ref. A-23, and A-25), particulate emissions were found to increase as underfire airflow was increased. Particulate discharge is essentially the same on a dry weight basis for both 25% and 50% moisture fuel levels at a given underfire air velocity. Increasing the fuel charging rate increases the particulate discharge per hour, but shows no effect on a lb. of particulate per lb. of fuel basis.

When the dry weight of fuel burned is used as the basis of comparison, the maximum produced by 25% moisture fuel is only 1.4 times the maximum resulting from 50% moisture fuel. The results are summarized below.

Test Conditions							
Excess Combustion Air %	Fuel Burned lb/hr	Air Distribution %			Stack Discharge, scfm	Particulates	
		Underfire	Secondary	Overfire		gr/scf	Lb/Ton Burned
50% Moisture Fuel							
50	140	60	20	20	184	0.037	0.83
					184	0.054	1.2
					200	0.019	1.2
		15	0	85	186	0.023	0.53
	240	60	0	40	322	0.074	1.7
					276	0.11	2.4
					289	0.031	0.64
		15	20	65	259	0.040	0.73
300	140	60	0	40	410	0.053	2.6
					428	0.017	2.4
		15	20	65	406	0.031	1.5
					398	0.023	1.1
	240	60	20	20	700	0.18	5.2
					618	0.073	3.2
		15	0	85	772	0.044	2.4
					530	0.032	1.2
25% Moisture Fuel							
50	140	60	20	20	233	0.33	9.4
					211	0.33	8.4
		15	0	85	228	0.019	1.4
					219	0.16	4.3
	240	60	0	40	440	0.13	4.0
					348	0.33	8.2
		15	20	65	364	0.044	1.2
					388	0.041	1.1
100	140	60	0	40	545	0.045	3.0
					568	0.016	3.2
		15	20	65	576	0.027	1.9
					553	0.030	2.0
	240	60	20	20	710	0.089	4.5
		15	0	85	920	0.075	4.9
					875	0.085	5.3
					915	0.052	3.4

Reference A-25 (1959)

This describes the first phase of a study carried out on an experimental incinerator to determine the effects of variation in combustion air distribution. (See Ref. A-23 and A-24) Particulates in the flue gas were sampled isokinetically at a representative point eight diameters downstream from the breeching and eight diameters upstream from the top of the stack. Solids were collected on an MSA type 1106-BH glass-fiber filter without organic binder. Mass determination of the solids was made on an analytical balance, and the volume of gas sampled was measured with a dry-type bellows meter. A calibrated orifice meter, preceding the gas meter, was used to control the instantaneous sampling rate. Corrections were applied for meter temperature, meter pressure, barometric pressure, and humidity.

Tests were limited to a uniformly prepared rubbish of 25% moisture content which was burned under closely controlled conditions of charging and air distribution in a fixed-dimension, multiple chamber incinerator.

One of the common concepts regarding particulate discharge from municipal incineration processes is that total solid emissions result solely from physical entrainment of particles in the gas stream, with particulate discharge increasing with increased gas velocity through the fuel bed. This study concluded that the concept of physical entrainment of solids as the sole mechanism for producing total solid emissions is not valid. While physical entrainment probably contributes to the discharge of particulates, other factors such as volatilization and condensation of inorganic compounds and incomplete combustion also affect the degree of this discharge. The following results were obtained.

TABLE 3A

Fuel Burned lbs/hr	Air Distribution Underfire 50% Excess	Overfire Air Level	Stack Discharge (Scfm)	Particulates (gr/SCF)	(lbs/ton burned
140	155	205	250	0.11	1.6
			240	0.044	1.5
			230	0.034	0.96
			230	0.068	1.9
	305		220	0.22	5.9
			270	0.13	4.1
			270	0.17	5.7
			250	0.21	6.4
	155		330	0.049	1.6
			320	0.10	5.2
			320	0.068	2.1
			300	0.057	1.6
	305	205	300	0.27	8.6
			310	0.086	2.5
			320	0.15	4.4
			330	0.072	2.5

TABLE 3B

Fuel Burned lbs/hr	Air Distribution Underfire 50% Excess	Overfire Air Level	Stack Discharge (scfm)	Particulates (gr/SCF)	(lbs/ton burned)
140	15%	0%	400	0.047	2.5
			390	0.042	2.0
			380	0.037	1.7
			440	0.037	2.0
	30%	20%	400	0.040	2.0
			370	0.035	1.6
			350	0.038	1.6
			370	0.024	1.6
	15%	20%	490	0.036	1.7
			480	0.035	1.6
			510	0.029	1.4
			490	0.014	1.6
	30%	0%	500	0.056	2.8
			530	0.0	2.1
			490	0.035	2.6
			450	0.036	2.6

Reference A-26 (1957)

A general discussion of incinerator testing and emission results is presented. Specific findings reported include: 1) incinerators lacking special fly ash collecting equipment emit an average of 20 lbs particulate/ton of refuse with a range of 10 to 26 lbs particulate/ton of refuse; 2) forced draft air systems double particulate emissions; and 3) there are approximately 16 lbs of stack gas per lb of refuse.

Reference A-27 (1953)

The results of tests made on municipal incinerators in Los Angeles County indicate 3.34 to 17.8 pounds of solids per ton of refuse burned; the average for 9 tests is 8.84 lbs/ton of refuse. The percentage of combustibles was 4 to 10 percent. 30 percent by weight of the solid particles were less than 5 microns in size. Four of the collected samples were analyzed, yielding the following:

Sample 1

This sampling train consisted of a precipitator, six impingers and a Millipore filter. A spectrographic analysis of the material collected in the precipitator thimble showed as follows. The amount collected in the precipitator thimble represented 77.6 percent of the total sample.

Large Amount (xx%)
- Sodium
- Potassium
- Calcium
- Aluminum
- Silicon

Small Amount (x%)
- Magnesium
- Iron

Very small Amount (.x%)
- Lead
- Titanium
- Zinc

Traces (.0x to .000x%)
- Barium
- Strontium
- Lithium
- Copper
- Chromium
- Manganese
- Tin

A chemical analysis of the cations and anions showed:

SiO_2	20.6%		Cl	12.2
R_2O_3	10.4		SO_4	16.8
Ca	2.7		PO_4	14.0
Mg	4.7	(max., cal. on basis of SO_4)	NO_2	0.5
			Combustibles	4.2
Na	4.1			
K	13.3			

The precipitator condensate, or the material that was collected in the impingers, representing 22.3 percent of the total sample, was also analyzed chemically. The results of these analyses were:

R_2O_3	2.2%	Ca	5.6
SiO_2	6.1	$Na+K+SO_4$	86.1 (by difference

Sample 2

The second of the four samples for chemical identification were taken using four impingers followed by a Millipore filter. The dissolved and undissolved material collected in the impinger train (84 percent of the total sample) were concentrated by evaporating the free moisture to dryness at 110°C. The analysis of the cations and anions showed the following:

SiO_2	13.8%	Cl	15.2
R_2O_3	5.7	SO_4	24.1
Ca	2.5	PO_4	11.4
Mg	4.7	NO_3	0.4
Na	4.2	Combustibles	4.2
K	11.7		

This analysis compares favorably with that of the precipitator sample of the first test of this series. Even though the SiO_2 and R_2O_3 are lower, they appear to be in the same relationship to each other.

The Millipore filter which followed the impingers collected the remaining 16 percent of the sample. The spectographic analysis of this material was as follows:

Large Amount (xx%)
  Sodium
  Potassium

Small Amount (x%)
  Calcium
  Lead
  Zinc

Very Small Amount (.x%)
  Magnesium
  Iron

Traces (.0x to .000x%)
  Barium
  Strontium
  Lithium
  Tin
  Copper
  Chromium
  Manganese
  Silicon

Sample 3 and 4

The third and fourth tests of this series were made using a Whatman thimble following four impingers. The small amounts of material collected in the Whatman thimbles in each test were not used in this analysis because it was impossible to accurately remove the material from the thimbles. The materials collected in all the impingers were combined for the following chemical analysis:

Analysis of Water Insoluble Portion

Water Insoluble Material....	1.9608 grams	
Acid Soluble		0.1509 grams
Acid Insoluble		1.8099 grams
Ash....................	1.2235 "	
Combustibles...........	0.5864 "	

Acid Soluble Analysis	
Iron	0.0671 "
Calcium	0.0350 "
Magnesium	0.0047 "
Phosphorus	Present

Analysis of Water Soluble Portion

Water Soluble Material (after drying)	4.1512 grams
Total Acid, as Sulfuric Acid	1.2315 "
Total Sulfates, as Sulfuric Acid	1.9659 "
Combined Sulfates	0.7344 "

Elemental Analysis of Water Soluble Portion

Chlorine	1.1504grams
Sulfates, as SO_3	1.6041 "
Nitrates	0.1537 "
Sodium	0.1794 "
Potassium	0.6966 "
Phosphorus	0.0174 "
Calcium	0.0631 "
Magnesium	0.0881 "
Iron and Alum, as R_2O_3	0.0475 "
Insoluble	0.0664 "

The total weight of the complete sample would thus be

Total Dried Solids	4.1512grams
Volatilized Chlorides	1.1504 "
Volatilized Nitrates	0.1537 "
Water Insoluble	1.9608 "
Material in Thimble	0.3340 "
Total	7.7501grams

Conclusions are:

1. Approximately 20 percent of the discharge is condensable, with approximately 5 to 15 percent as SO_3.

2. Approximately 80 percent is particulates containing silicon, lead, aluminum, calcium and iron. Since these constituents exist in the atmosphere in aerosol form, they contribute to the reduction in the visibility. It has been shown that as the particles in the 0.5 to 0.8 micron range increase relative to other sizes, the visibility decreases in Los Angeles County.

3. Approximately 2/3 of the total sample collected is water soluble.

4. Approximately 30 percent by weight of the sample is below 5 micron in size.

5. Approximately 4 to 10 percent of the solid particulate matter is combustible.

6. The solids emitted into the atmosphere from properly designed municipal incinerators can be as much as an 80 percent improvement over that from backyard types.

2. Discussion

Although there are many references to particulate emission levels, there does not seem to be very good agreement among the data. In particular, there is very little discussion of particulate sampling procedures employed for specific reported emissions. Additionally, there is a consistant lack of descriptive data on incinerator operating parameters, antipollution control devices employed, combustion practice, etc. A second area of uncertainty relates to definitions or terminology of "solid particulate", "fly ash," "combustibles," "condensibles," and "residues." These terms are often used interchangeably which causes confusion in data interpretation. A third area, in which only cursory discussion is presented, concerns particulate analysis. Emissions are reported on a mass basis and, in some cases, fly ash chemistries and particle size distributions are given. There seems to be no use of the more sophisticated characterization methods such as scanning electron microscopy to measure the size and shape of individual particles and to identify particle agglomorates, electron probe microanalysis to measure the chemistry of individual fly ash particles, or electron diffraction to identify crystalline phases present in fly ash. As a result, the reported emissions can only be treated in a qualitative way.

Another area of concern that is not discussed in the literature is chemical interactions due to the residency of collected particles in the sampling apparatus. For example, is the fly ash collected on a filter altered to carbonates and sulfates by the passage of wet flue gases? Is the particle size distribution altered by agglomeration or by coalescence of particles?

Finally, there is essentially no discussion of condensed particulates. The recent paper by Achinger and Daniels (Reference A-11) and the early paper by Chass and Rose (Reference A-27) give the only reports of impinger catch chemistries. There is insufficient data to evaluate chemical reactions which may possibly occur between impinger liquids and the gas effluent.

There is specific need for more quantitative data on the chemistry and particle size distributions of solid particulates so that the efficiencies of anti-pollution control devices can be more carefully evaluated.

B. Carbon Oxides (N_2,O_2)

1. Bibliography

Reference A-11 (1970)

Integrated gas samples were collected in a flexible bag sampler and analyzed with the use of an Orsat analyzer. Instantaneous grab samples were also taken during each stack test and analyzed with a manual wet-chemistry carbon dioxide indicator.

Sampling was done at a number of different types of municipal incinators with various kinds of APC devices. The composition of the refuse burned at each incinerator is detailed. CO_2 levels ranged from 2.8 to 5.0 percent with excess air values of 200 to 500 percent. No correlation existed between CO_2 levels and percentage excess air.

Reference A-28 (1970)

This paper describes experimental incineration of widely-used disposable container plastics, and describes the sample train used to test the resulting effluent. High proportions of CO and CO_2 were reported. The furnace used was a tightly-controlled experimental one. Volatile combustion products were collected in Saran bags attached to the end of the combustion tube, which protruded about 6" past the furnace. Analyses of major products were done by infrared spectroscopy. Minor components sometimes required gas chromatography.

Reference A-2 (1968)

Municipal incinerators are reported to emit one pound CO per ton of refuse.

Reference A-17 (1967)

This paper describes parts of a program designed to compare the composition of stack emissions from several New York City area incinerators. The sampling train includes a probe with which embodies a filter for particulates, two large volume and one small volume, specially-designed coil traps. During operation, the first two coil traps are maintained at 0°C and the third at -78°C (with dry ice-acetone). This procedure was employed to freeze out and condense various organic species. Representative samples of gaseous components are collected in flush-thru gas sampling tanks.

The high collection efficiency of the trapping system was demonstrated in experimental runs. Two tests yielded 5.73% CO_2 and 0.046% CO for 12.8% O_2, and 7.4% CO_2 and 0.090% CO for 11.6% O_2.

Reference A-16 (1967)

This paper describes the results of studies at a municipal incinerator in New York. All testing was conducted in accordance with the ASME Test Code PTC-21 (1941) and PTC-27 (1957). Average Orsat analyses for a series of 10 tests yielded: CO_2 - 3.2 to 4.2%; O_2 - 15.2 to 16.0%, CO - 0.0 to 0.1%; and N_2 - 79.7 to 81.0%; excess air levels ranged from 242 to 313%.

As an example of the APC devices involved, #3 incinerator in this study included a secondary combustion chamber, a low velocity expansion or cooling chamber, 4 banks of high pressure water sprays, a secondary baffle chamber, and cyclone collectors. Testing location: openings constructed in the chimney walls at a point 129 ft. above the base of the 265 ft. stack.

Reference A-29 (1966)

In a multiple chamber incinerator, there was emitted 0.7 lb CO/ton of refuse. However, no sampling or analysis data were given.

Reference A-20 (1964)

Selected tests on multiple chamber incinerators yielded 6.2 to 8.7 CO_2 and 11 to 13.7 O_2 in the breeching and 3.7% CO_2 and 16.7% O_2 in the stack; CO levels were to 1 to 4 lbs./ton of refuse and 2 lbs./ton of refuse (max.) respectively.

CO_2, O_2, CO and total gaseous hydrocarbon concentrations were measured by collecting a 50 to 100 liter sample of the combustion gases in a Mylar plastic bag and subjecting this sample to individual analyses. Integrated samples were obtained by maintaining a flow of one liter per minute or lower of sample gas to the bag over a one- to three-hour period simultaneous with the poly-nuclear hydrocarbon sampling. Where different modes of operation yielded more than one flue-gas flow rate in the stack, the sample flow rate to the bag was adjusted proportionately.

CO_2 was analyzed by Orsat and checked with a nondispersive infrared analyzer; O_2 was measured by Orsat and a paramagnetic type O_2 analyzer; CO was measured by a nondispersive infrared analyzer and gas detector tubes.

Emissions of total gaseous hydrocarbons were plotted against carbon monoxide emissions; the least-squares line drawn through the points has a correlation coefficient of 0.71 (significant at the 1.0% level). A better correlation between CO and total gaseous hydrocarbons was not expected in view of the variety of types of combustion processes involved.

Hydrocarbons are more susceptible to oxidation and decomposition at high temperatures than is carbon monoxide. Accordingly, the hydrocarbon emission rates are lower than those for CO, and in general the ratio of the total gaseous hydrocarbon emission to the CO emission is lower for the larger incinerators.

Reference A-9 (1964)

Analyses of the components of municipal refuse were assembled, from which an average composite analysis was calculated. The analyses of the flue and stack gases from 18 municipal incinerators were also tabulated and plotted. A marked difference was noted between the analyses of the stack gases and those to be expected from the combustion of the composite refuse. Much of the difference can be accounted for by the carbon loss in the residue and oxidation of metallics. Suggestions for future investigations include new refuse and residue analyses, and chemical studies on the interaction of spray water and fly ash with flue gas.

Calculated gas analyses based upon refuse compositions are:

Air Supplied	Dry Volume, Per Cent CO_2	O_2	N_2	C/(H)
Theoretical	19.62	0.00	80.38	36.3
100 per cent excess	9.73	10.56	79.71	37.7
200 per cent excess	6.47	14.08	79.50	38.1
300 per cent excess	4.85	15.76	79.39	39.4
400 per cent excess	3.87	16.81	79.32	41.2

Assuming 20 percent carbon in the residue and partial oxidation of metals, the calculated flue gas composition becomes:

Air Supplied	Dry Volume, Per Cent CO_2	O_2	N_2	Apparent C/(H)
Theoretical	18.80	0.00	81.20	21.2
100 per cent excess	9.27	10.61	80.12	21.6
200 per cent excess	6.15	14.09	79.76	22.1
300 per cent excess	4.61	15.80	79.59	22.3
400 per cent excess	3.68	16.84	79.48	22.7

In practice, 35 tests on incinerators with dry gas systems yielded an excess air level of 145 to 771 percent with an average of 324 percent. The average gas analysis was 3.88 CO_2, 16.15 O_2, 0.03 CO, 79.94 N_2 and C/(H) of 10.8. Thirty nine tests on incinerators with wet after chambers had a range of 115 to 965 percent excess air, with an average of 266 percent. Gas analysis was 4.69 CO_2, 15.38 O_2, 0.13 CO, 79.82 N_2 and C/(H) of 14.9.

Precautions are given for gas sampling and analysis:

1. Use a water-jacketed sampling probe when withdrawing flue gas from furnaces and other hot zones. A hot low carbon or stainless steel or a copper tube can be oxidized by the flue gas, which will reduce the oxygen content appreciably. Also, the water cooling will help quench combustion of CO and H_2 that may be present in the gases.

2. When collecting gas samples over liquid, use a liquid that will not react with or absorb any of the sample. Saturated NaCl brine, mercury or saturated water solution of sodium sulfate acidulated with sulfuric acid are satisfactory. Tap water absorbs CO_2 readily, causing serious error. Gas-saturated tap water readily evolves or absorbs gas with changes of temperature and gas composition.

3. Gas compositions fluctuate rapidly with time, and will vary across furnaces and passages. A gas sample represents only the gas flowing past the end of the probe during the period of sampling. Stratification is least in the stack and particularly after a dust collector or induced-draft fan. However, mixing in passage does not eliminate fluctuations based on time cycles, such as in batch furnaces. Numerous gas samples are usually required, each analyzed carefully.

4. The Orsat apparatus works best at normal room temperatures. Low readings for O_2 are obtained at 40-60°F. The solutions must be kept out of the manifold piping, and must be washed out if accidentally allowed to contaminate the bores. A gas sample should not be admitted to the apparatus until the manifold is filled with nitrogen remaining from a previous analysis of gas or air.

The following conclusions are reached:

1. The flue-gas analyses calculated for the probably refuse had an apparent C/(H) ratio of 15.5 at 300 percent excess air. The drop from 24.1 to 15.5 was the result of an allowance for an estimate 20 percent carbon in the total residue and a 54 percent oxidation of the metals in the refuse. The result approximates the average of actual flue gases from municipal incinerators.

2. The analyses of gas samples taken at the inlets and outlets of dry separation chambers indicated the combustion of much carbon and some carbon monoxide in the dry separation chambers. Char flakes are deposited in a hot zone and continue to glow and burn over an extended period of time. The median C/(H) ratios increased from 7.3 to 17.1 in the plants from which data were available. Hydrocarbons may also have burned in the dry chambers but to a minor degree in comparison with carbon.

3. During passage through wet separation chambers the changes in flue gases showed relatively more combustion of hydrogen and hydrocarbons than of free carbon. Char flakes were probably burned more slowly and were quenched before they had an opportunity to burn out. Between the furnace outlets and the spray chamber outlets the median C/(H) of the gases dropped from 17.5 to 11.8. Most of this change probably occurred in the passage between the furnace exit and the inlet to the wet chamber.

4. While flue gases undoubtedly react chemically with the unevaporated spray water and wet fly ash, the effect on the flue gas analysis appears to be slight. Research in this area would be advisable.

Reference A-22 (1962)

Field tests were conducted on two different size full-scale incinerators (50- and 250-tons/day). On both, the concentration of CO was too low to be measured using the Orsat technique. The 50-ton/day incinerator gave readings slightly above the limit of detectability on a nondispersive infrared gas analyzer having a full-scale range of 0 to 5%. The 250-ton/day incinerator CO was measured with a stain-in-tube type gas detector with a detection range of 10 to 2000 ppm.

The 50-ton/day incinerator, at lowest average temperature, produced the highest CO emission: 1.0 lb/1000 lbs. dry flue gas.

The 250-ton/day incinerator, with high temperatures and high excess air levels, produced 0.03 to 0.07 lb. CO/1000 lbs. dry flue gas.

Reference A-30 (1962)

Methods of sampling and analysis were developed by the APC District of Los Angeles. The sampling train consisted of a miniature glass cyclone separator, an alundum filter thimble, two or more wet impingers and a dry impinger with a thermometer which was used for obtaining vapor content of the water saturated effluent gas. An integrated gas sample is taken during the test for carbon dioxide analysis.

Reference A-23 (1960)

In a special study measuring stack effluents resulting from incineration of a high volatile fuel component (asphalt saturated felt roofing), particulate and gas emissions were measured as a function of fuel feed rate, charge size and percent excess air. The experimental setup is the same as described in Reference A-25.

Sampling was done with continuous measurement by nondispersive infrared gas analyzers supplemented with strip chart recorders for CO and CO_2. Oxygen was measured on a continuous basis using an instrument operating on the paramagnetic properties of oxygen.

All values reported herein are the averages of intermittent surges which occurred for brief intervals (up to 50% of fuel charging cycle) immediately after fuel was charged. Maximum peak concentrations ranged up to five percent CO. Under the variety of conditions tested, this study found 0 - 143.5 lb. CO/ton of fuel and 3.9% - 10.9% average O_2 - CO_2. The CO levels were negligible for excess air levels greater than 100%.

Reference A-24 (1960)

The paper describes additional studies carried out on the experimental incinerator set-up described in Reference A-25.

The thermal conductivity type analyzer used for CO_2 measurement was replaced with a nondispersive infrared gas analyzer, with a range of 0 to 18% CO_2 and operated at a wave length of 4.29 microns. CO was measured continuously with a positive type nondispersive infrared analyzer with a range from 0 to 14%. O_2 content was determined with an instrument employing principles based on the paramagnetic properties of oxygen.

The CO content of the stack gases followed exactly the same pattern as the hydrocarbons. With 50% moisture fuel, the CO concentration was 0.12% (30 lbs per ton fuel) at 300% excess air and 0.11 (12 lbs per ton fuel) at 50% excess air. A maximum concentration of 2% CO was produced when oxygen level dropped to 3%. With 25% moisture fuel, the CO concentration was 0.09% (29 lbs per ton fuel) at 300% excess air and 0.13% (19 lbs per ton fuel) at 50% excess air. CO production occurred uniformly at 300% excess air, but intermittant peaks of short duration occurred at 50% excess air immediately after introduction of the fuel.

Reference A-25 (1959)

A small, experimental, refractory-lined, multiple-chamber prototype incinerator was employed to measure stack emissions under a variety of experimental conditions. A detailed description of the incinerator and sampling train is given: O_2 and CO_2 were continuously measured. CO content was measured by passing a continuous stream of effluent gas through a positive type nondispersive infrared gas analyzer, employing a diaphragm cell, with a range from 0 to 5% and operating at a wave length of 4.4 4. Tests were limited to a uniformly prepared rubbish of 25% moisture content.

Except for one unexplainable occurance of CO on a duplicate test, all conditions of combustion at the 150% excess air level failed to produce CO in excess of the 0.1% lower limit of detectability. Combustion at the 50% excess air level produced intermittant surges of CO. (This paralleled the occurance of hydrocarbons). CO discharges are a function of proper employment of combustion air as it relates to distribution within the ignition chamber and levels of oxygen available in the combustion zone.

Reference A-18 (1957)

In two multiple chamber incinerators, CO_2 was found at 6.3% and 6.4% dry basis. An integrated gas sample for Orsat analysis is collected by withdrawing gases continuously from the stack at a constant rate by a liquid displacement method. A 5 liter bottle filled with a saturated sodium sulfate solution, acidified with sulfuric acid, is used as the collecting gas holder. As the solution siphons out the gas sample is drawn into the bottle. The rate of siphoning is adjusted so that a gas sample of about 4 liters is obtained during the course of the test. The sample is drawn from the stack at the same cross section used for collecting the combustion contaminants.

This reference contains specific discussions and explanations on the location of testing equipment, number and variety of sampling holes in the stack, isokinetic flow, sampling rate, and meter conditions. Data from an actual test on a municipal incinerator is used to demonstrate step-by-step the calculations made, with descriptions and equations.

Reference A-26 (1956)

A series of 6 tests on a unspecified incinerator yielded the following Orsat analyses: 6.13% - 6.75% CO_2, 13.43% - 14.20% O_2, and 0.10%-0.20% CO.

Measurements of the sampled gas volume involved the use of calibrated pressure drop methods, Flowrotor, and velocity determinations. These were always double or triple checked. This study was mainly concerned with particulate emissions.

Reference A-27 (1953)

In a summary of incinerator discharges in the Los Angeles area, the CO_2 levels of 9 incinerators ranged from 5.5 to 8.9% (dry basis). The major emphasis in this study was particulates, and not much specific information is given on the sampling and analysis of gaseous effluents.

Reference A-31 (1967)

For a typical refuse composition (4500 BTU/lb.) and combustion with 200% excess air, the author calculates the following stack gas concentrations: CO_2 - 1738 lbs./ton (6.05% dry volume), CO- 10 lbs./ton (0.06% or 600 ppm) and O_2 - 2980 lbs./ton (14.32%).

2. Discussion

Most measurements of major combustion gases are made continuously by Orsat analysis. These gases include CO_2, N_2, O_2 and sometimes CO. Orsat analysis has a typical sensitivity of ± 0.1 percent, which is comparable to the reported range of CO emission levels. Thus, there is a question of data credibility due to unintentional human bias in making readings.

Several authors have reported a change in CO emissions of up to 100 times increase immediately after charging in a batch type incinerator. This effect must be kept in mind during sampling to insure a representative measurement of CO emissions.

C. Sulfur Oxides

1. Bibliography

Reference A-32 (1969)

It is reported that SO_x emissions are not affected by incinerator design; they are a direct function of the sulfur content in the refuse burned. Values given for emissions from multiple chamber incinerators are: SO_2 - 1.7 lbs/ton of refuse burned; SO_3 - 0.1 lbs/ton of refuse burned.

Reference A-2 (1968)

In a summary of emission data from municipal incinerators, SO_2 levels are reported to be 2 pounds per ton of refuse.

Reference A-33 (1968)

Determination of sulfur dioxide, sulfur troxide, or sulfuric acid mist becomes difficult in the presence of other acid gases or where collected samples are highly colored or turbid. A method is described by which all oxides of sulfur are oxidized and precipitated as barium sulfate. The barium in the precipitate is determined by measuring the intensity of the L-alpha emission produced by x-ray excitation. The method is useful for about 0.05 to 10 micromoles of oxides of sulfur in the aliquot analyzed.

Reference A-34 (1968)

In Europe (West Germany), municipal incinerator refuse is generally 70% domestic and 30% industrial waste. Sulfur contents of the refuse are typically 0.3 percent. SO_2 emissions range from 0.122 to 0.286 grains/SCF; 15-20% of the sulfur is emitted as SO_3.

Reference A-14 (1968)

Typical U. S. refuse (containing 28% moisture and 22% inerts) has a sulfur content of 0.1%. The author has used test data from several sources to evaluate sulfur emissions. Although there is a wide spread of data, he concludes that 25% is emitted as SO_2, 25% is tied up as sulfate in fly ash and 50% is present as sulfate in the ash residue. In a series of 27 tests carried out on four California incinerators, SO_2 levels were 1-100 ppm at 5% CO_2; the median SO_2 levels was 17 ppm. The sulfate content of fly ash is dependent on the percentage of alkaline oxides (Na_2O and K_2O). In a series of tests, the SO_3 level of fly ash increased from 1.2 percent (collected over the incinerator bed) to 7.2 percent (collected in the stack). The alkaline oxide levels increased proportionately.

Reference A-31 (1967)

In a general discussion of incineration, the author claims that 0.1%S is normal refuse (equivalent to 1 lb. sulfur/ton refuse) results in 1 lb/ton SO_2; the remaining sulfur (75%) is fixed as sulfate in the fly ash and residue.

Reference A-35 (1967)

Low SO_2 emissions are due to low levels of sulfur in refuse (i.e., 0.1 percent) and competing reactions to form sulfate in fly ash and residue.

Reference A-36 (1966)

The author gives typical SO_x (reported as SO_2) emissions from incinerators as 20-460 ppm with an average of 250 ppm.

Reference A-20 (1964)

Sampling for SO_x analyses is described. The gas stream is passed through a series of three 500 ml Greenburg-Smith impingers containing a 3% solution of H_2O_2. Sampling is at 1 cfm for 20 to 40 minutes. Analysis is gravimetric (precipitating sulfate as barium sulfate) or by titration of an aliquot with barium chloride with thorin as an indicator.

There is no discussion of incinerator SO_x emissions.

Reference A-37 (1962)

Data collected from several published sources is compiled. The following SO_x levels (reported as SO_2) are given: incinerator with spray chamber-36 ppm; three incinerators with scrubber-0-32 ppm; three incinerators without scrubber-11-60 ppm. There is no discussion of the data collection.

Reference A-18 (1957)

Provides sampling and analysis procedures for SO_2 and SO_3 as follows: The sample train consists of a paper thimble maintained just above the dew point of the stack gases followed by 3 series-connected impingers immersed in an ice bath, a dry gas meter and a pump. The thimble acts as a collector for the sulfuric acid aerosol formed from the sulfur trioxide. The first 2 impingers contain 100 ml each of approximately 5% sodium hydroxide solution. The third impinger is dry. The sulfur dioxide gas passes through the thimble and is collected in the impingers. The thimble is extracted with hot water and the solution is titrated with standard sodium hydroxide solution to determine the sulfur trioxide. The sulfur dioxide collected in the impingers is determined by oxidation with bromine, acidification, and precipitation as barium sulfate. For a single chamber incinerator, the following test results are given: SO_2 - 2.3 and 1.4 lbs/ton of refuse burned; SO_3 - nil and 0.5 lbs/ton of refuse burned.

Reference A-38 (1954)

In 1950, a specific Los Angeles incinerator produced 1.9 lbs SO_2/ton of refuse burned. They reported that 20 percent of the total emissions were condensible, with 5 to 15 percent being SO_3.

2. Discussion

Among the papers surveyed, there was no complete discussion of SO_x emissions, including incineration parameters, sampling procedure and analysis methodology. It is therefore difficult or impossible to judge the reliability of the reported data. Most papers report SO_2 levels in ppm; these cannot be directly compared, however, for the basis of measurement (i.e., percent excess air) is generally not stated. It appears that there has been no attempt to measure sulfur mercaptans, such as H_2S. In general, SO_x emissions do not seem to be considered important due to the relatively low level of sulfur in refuse.

Based upon our review of the literature, we infer that about half of the sulfur in the refuse is collected in the fly ash, the wet scrubbers and the incinerator residue, the remainder being emitted as SO_2 and SO_3.

D. Nitrogen Oxides

1. Bibliography

Reference A-13 - 1968

The author claims that nitrogen oxides are not of concern in refuse burning since temperatures required for their formation (significantly above 2000°F.) are not attained in municipal incinerators.

Reference A-29 - 1968

The author found 2.1 lb. NO_x/ton of refuse. No sampling or analysis methods are given.

Reference A-2 - 1968

In a summary of emission data from municipal incinerators, NO_x levels are reported to be 2 lbs./ton of refuse.

Reference A-31 - 1967

Typical nitrogen oxide levels in incinerator emissions correspond to 3 lbs/ton of refuse (93 ppm, percent dry volume). There is no discussion of sampling or analysis methods. Typical refuse analysis yields 0.5% by weight nitrogen (10 lb/ton of refuse).

Reference A-17 - 1967

Equipment was prepared for gas analysis of incinerator stack effluents in the New York City area. Nitrogen oxides were to be analyzed according to PHS Publication No. 99-AP-11 "Selected Methods for the Measurement of Air Pollutants", May, 1965. No nitrogen oxides emissions data are given.

Reference A-20 - 1964

In three tests, NO_2 was 2.5 lbs/ton of refuse in a 250-ton/day incinerator (sample taken before settling chamber). In a 50-ton/day incinerator, there were 2.4 lbs. NO_2/ton of refuse before the scrubbers and 2.8 lbs. NO_2/ton of refuse after scrubber. Oxides of nitrogen are produced by the burning of all waste materials regardless of the quality of the combustion process. (This is different from Ref. A-14's view on preceeding page). NO_x concentrations were measured from two-liter integrated samples, and analyzed either by the Saltzman or the phenoldisulfonic acid technique. The Saltzman technique was not satisfactory for analyzing samples from units that burn fuel with significant sulfur content because of serious interference from sulfur dioxide.

Reference A-22 - 1962

A series of field tests were made on various-size full-scale incinerators. Both sizes (50- and 250-ton/day) showed the same emission rate for NO_x; NO_2 emission increased at higher excess air levels. With low underfire and high overfire air, higher NO_2 levels resulted (because oxygen consumption is slower, and the air exists in the high temperature zone at a comparatively high O_2/N_2 ratio for a longer time.) The following data were reported:

Combustion Conditions			Emissions	
Underfire Air -%	Excess Air -%	Temp. Secondary Chamber	Before Scrubber	After Scrubber
50 Ton/Day Batch Charge Incinerator				
20	235	1080	0.38*	0.46*
50	110	110	0.28	0.25
70	100	100	0.16	0.23
20	215	---	3.2**	3.3**
55	110	---	2.3	2.3
60	100	---	1.4	2.2
250 Ton/Day Continuous Charge Incinerator				
20	190	1750		0.33* (3.0**)
50	180	1790		0.27 (3.1)
80	190	1930		0.22 (2.2)
100	.50	1900		0.20 (2.5)

* Pounds NO_x (as NO_2)/1000 Pounds dry flue gas (corrected to 50% excess air)

** Pounds NO_x (as NO_2)/Ton of Refuse Burned.

Reference A-30 - 1962

This study used methods of sampling and analysis developed by the Research Division of the APC District, Los Angeles County: single chamber incinerator = 0.1 lbs. NO_2/ton of fuel, multiple chamber = 2.1 lbs. NO_2/ton of fuel. Oxides of nitrogen have little relation to the waste material composition, and tend to be formed in proportion to incinerator operating temperatures. Thus, multiple chamber incinerators, with higher temperatures, form more NO_x.

Reference A-23 - 1961

For this study, these were done on an experimental incinerators. Incinerator operating parameters, including excess air, fuel feed rate, lb. fuel per charge, and under- and over-fire air, were varied in a controlled way. NO_2 ranged from 1.8 lb. to 5.7 lb./ton of fuel, in a series of thirty tests. NO_x were measured by Saltzman modification of the Griess colorimetric method and expressed as equivalent NO_2. Samples were collected in evacuated flasks containing the liquid reagent. The following results were obtained:

Excess Combustion Air	Fuel Feed Rate (lb/hr)	Air Distribution Underfire	Overfire	Second-are	NO_2 Lb/Ton Fuel
50%	150	80%	20%	0	1.8
		89%	20%	0	2.1
100%		15%	85%	0	5.2
		22 1/2%	77 1/2%	0	4.2
		60%	40%	0	4.0
		90%	10%	0	3.8
		15%	85%	0	4.7
		60%	40%	0	3.3
	150	15%	85%	0	4.1
		60%	40%	0	4.5
		60%	15%	25%	3.6
		15%	85%	0%	3.8
		60%	40%	0	3.9
		60%	15%	25%	3.6
150%	150	12%	68%	20%	4.2
		48%	12%	40%	4.4
		48%	12%	40%	4.4
200%	100	15%	85%	0	4.4
		60%	40%	0	4.4
		15%	85%	0	4.3
		60%	40%	0	4.7
	150	10%	90%	0	5.2
		15%	85%	0	4.7
		40%	60%	0	5.6
		40%	40%	50%	4.5
		60%	40%	0	3.0
		15%	85%	0	4.4
		60%	40%	0	5.7
300%	100	15%	85%	0	3.0
		60%	40%	0	3.4

Reference A-24 - 1960

The same small experimental incinerator described in References A-23 and A-25 was used in this study, which sought to determine the effects of fuel moisture content on pollutant emissions, while varying the amount of fuel charged per hour.

Oxides of nitrogen, expressed as NO_2, were determined by the Griess colorimetric method as modified by Saltzman. On tests with 50% moisture fuel, average NO_2 concentrations were determined by taking up to ten instantaneous grab samples over two or three burning cycles. On tests with 25% moisture fuel, integrated samples were collected over two or more fuel charging cycles. The two methods gave comparable average NO_2 values when used with identical test conditions. The results are summarized as follows:

Excess Combustion Air	Fuel Burned lb/hr	Underfire	Secondary	Overfire	Stack Discharge (sefm)	Nitrogen Oxides ppm	Nitrogen Oxides lb/ton Burned
50% Moisture Fuel							
50	140	60	20	20	184	101	1.9
					184	108	2.0
					200	121	2.5
		15	0	85	186	128	2.2
	240	60	0	40	322	100	3.1
					276	139	2.3
					289	132	2.3
		15	20	65	259	144	1.8
300	140	60	0	40	410	61	2.7
					428	68	3.0
		15	20	65	406	.86	3.6
					398	77	3.1
	240	60	20	20	700	67	2.8
					618	73	2.7
		15	0	85	772	66	3.0
					530	83	2.6
25% Moisture Fuel							
50	140	60	20	20	233	89	2.1
					211	98	2.3
		15	0	85	228	102	2.5
					219	90	2.2
	240	60	0	40	440	106	3.0
					348	---	---
		15	20	65	364	106	2.5
					388	119	2.6
100	140	60	0	40	545	47	2.8
					568	42	2.6
		15	20	65	576	46	2.9
					553	52	3.2
	240	60	20	20	710	50	2.3
		15	0	85	920	47	2.8
					875	58	3.2
					915	61	3.6

Geometric Mean of Nitrogen Oxides for 25% and 50% Moisture Fuel Tests on Both Wet and Dry Bases

Moisture Content of Fuel		Lb $NO_x/10^4$ Lb Fuel as Fired		Ratio	Lb $NO_x/10^4$ Lb Dry Fuel		Ratio
		50%	25%	25/50%	50%	25%	25/50%
Excess combustion air	50%	1.40	1.24	1.1[a]	2.20	1.65	0.8[a]
	300%	1.40	1.45	1.0	2.92	1.93	0.7[a]
Underfire air	15%	1.28	1.39	1.1	2.56	1.72	0.7[a]
	60%	1.26	1.29	1.0	2.52	1.88	0.7[a]
Secondary air	0	1.32	1.41	1.1	2.64	1.69	0.7[a]
	20%	1.22	1.27	1.0	2.44	1.69	0.7[a]
Fuel feed rate, lb/hr	140	1.28	1.27	1.0	2.56	1.69	0.7[a]
	240	1.26	1.41	1.1[a]	2.52	1.88	0.7[a]

[a] Indicates statiscally significant difference at 95% confidence level.

Reference A-25 - 1959

This study was done on the same multiple chamber experimental incinerator as described in References A-23 and A-24. Oxides of nitrogen, expressed as NO_2, were determined by the Griess colorimetric method as modified by Saltzman. For this determination, grab samples of the flue gases were collected in evacuated flasks containing Saltzman reagent. An average value of nitrogen oxides concentration, representative of operating conditions, was obtained by integrating beneath the nitrogen-oxides time-of-sampling curve. Preliminary studies indicated that the larger portion of nitrogen oxides in the stack effluent were in the form of nitric oxide.

Variables found to be most significant in the formation of NO_x were temperature, excess air and feed rate (grate loading); not significant were pounds of fuel/charge, stoking interval, % secondary air, and % underfire air.

Concentration of NO_x did not increase linearly with temperature, but as a logarithmic function of temperature. Ignition-zone temperatures are controlling. Other conditions being equal, increased operating temperature results in increased formation of NO_x. Typical levels of nitrogen oxides (reported as NO_2) are 30 to 40 ppm at 1000°F. and 80 to 90 ppm at 2000°F. Variations in excess air and refuse feed rate produced a smaller effect, with NO_2 values of 1.9 to 2.1 lbs./ton of refuse (28 to 34 ppm). A summary of results is presented below.

Fuel Burned lbs/hr	Air Distribution % Underfire	Air Distribution % Overfire	Stack Discharge	Nitrogen Oxide Emissions ppm	Nitrogen Oxide Emissions lbs/ton burned
50% Excess Air					
140	15	20	250	80	2.1
140	15	20	240	83	2.0
140	15	20	230	66	1.6
140	15	20	230	74	1.7
140	30	0	220	69	1.6
140	30	0	270	65	1.8
140	30	0	270	74	2.1
140	30	0	250	65	1.6
180	15	0	330	62	1.6
180	15	0	320	79	2.0
180	15	0	320	78	2.0
180	15	0	300	85	2.0
180	30	20	300	79	2.1
180	30	20	310	95	2.3
180	30	20	320	91	2.3
180	30	20	330	75	2.0
150% Excess Air					
140	15	0	400	51	2.1
140	15	0	390	53	2.1
140	15	0	380	63	2.4
140	15	0	440	64	2.9
140	15	0	400	48	1.9
140	15	0	370	54	2.0
140	15	0	350	63	2.2
140	15	0	370	52	2.0
180	15	20	490	75	2.9
180	15	20	480	60	2.2
180	15	20	510	47	1.9
180	15	20	490	66	2.6
180	30	0	500	60	2.4
180	30	0	530	55	2.3
180	30	0	490	54	2.1
180	30	0	450	58	2.1

Reference A-18 - 1957

The author reports measured NO_x levels of 3.9 to 4.6 lbs/ton of refuse for a single chamber incinerator. Samples for oxides of nitrogen were collected in evacuated bulbs. At least four samples were taken during a 1 hour test period. The bulbs for oxides of nitrogen contain a mixture of hydrogen peroxide and 0.1N sulfuric acid. Oxides of nitrogen are determined by the phenol disulfonic acid method and reported as nitrogen dioxide. Both the nitric oxide and nitrogen dioxide which may be present are measured by this method.

2. Discussion

The literature contains numerous reports of nitrogen oxide emission levels. Samples are generally collected in grab bottles and analysed by the phenol disulfonic acid method. This method does not distinguish between NO and NO_2. Emissions are believed to be quite constant with time, showing reductions after charging in batch process incinerators due to a lowering of the combustion temperature. High temperatures (~2000°F) are required for rapid production of nitrogen oxides. Niessen (A-1) reports 440 ppm nitrogen oxides are formed at 2000°F (100% excess air) and 7 ppm at 1100°F (300% excess air). Although NO and NO_2 are unstable at ambient temperatures, the rates of dissociation are so slow that there is little change in composition during residency in the incinerator and stack.

Potential interactions of NO and NO_2 with other incinerator effluents has not been treated in the literature.

E. Hydrocarbons

1. Bibliography

Reference A-2 - 1968

In a summary of emissions from municipal incinerators, the level of hydrocarbons (reported as hexane) is reported as 0.3 pounds per ton of refuse.

Reference A-22 - 1962

For comparison to laboratory studies (Ref. A-24 and A-25), a series of field tests were made on full scale incinerators. The total organic content of flue gases in a 250 ton/day incinerator was continuously monitored using a nondispersive hexane sensitized infrared gas analyzer. All tests showed hydrocarbon below the 15 ppm limit of detectability.

On a 50 ton/day incinerator, integrated bag samples were analyzed by a flame ionization detector with a sensitivity of 4 ppm carbon (0.7 ppm hexane). Hydrocarbon concentrations were below the 4 ppm carbon limit of detectability. The total hydrocarbon emissions rate of this incinerator for a variety of operating conditions was therefore less than 0.003 lbs/ 1000 lbs. dry gas. A 250 ton/day continuous feed incinerator yielded less than 0.08 lbs. hydrocarbons (as hexane) per 1000 lbs. dry gas.

Reference A-23 - 1961

Grab samples of incineration flue gases taken during hydrocarbon surges were analyzed by gas-liquid partition chromatography. Components identified included acetylene, ethylene, ethane, propylene, and benzene. Acetylene and ethylene predominated.

Tests were done on a multiple-chamber experimental incinerator (the same used in Reference A-24 and A-25. Fuel used in this test was asphalt saturated felt roofing cut into four-inch squares. The results are presented on the next page.

Excess Combustion Air	Fuel Feed Rate (lb/hr)	Air Distribution-%			HC Lb/Ton Fuel
		Underfire	Overfire	Secondary	
50%	150	80	20	0	3.8
		80	20	0	6.5
100%	100	15	85	0	0.0
		22 1/2	77	0	0.7
		60	40	0	0.4
		90	10	0	1.3
		15	85	0	3.4
		60	40	0	13.4
	150	15	85	0	0.0
		60	40	0	0.3
		60	15	25	0.3
		15	85	0	0.6
		60	40	0	4.9
		60	15	25	1.4
150%	150	12	68	20	0.0
		48	12	40	0.0
		48	12	40	0.4
200%	100	15	85	0	0.0
		60	40	0	0.0
		15	85	0	0.0
		60	40	0	0.7
	150	10	90	0	0.0
		15	85	0	0.0
		40	60	0	0.0
		40	10	50	0.0
		60	40	0	0.0
		15	85	0	0.0
		60	40	0	1.9
300%	100	15	85	0	0.0
		60	40	0	0.0

Reference A-39 - 1960

Gas chromatography was employed to measure C_2 to C_6 hydrocarbons for comparison to other analysis methods and to a proposed regulation limiting C_2 to C_6 hydrocarbons to 50 ppm. The following data are reported:

Gas Chromatographic Analysis of C_2 to C_5 Hydrocarbon in Incinerator Effluents

Concentration, ppm

Test No.	Type[a]	Acetylene	Ethylene	Ethane	C_3	C_4	C_5	C_6	Total C_2 to C_5 Hydrocarbons	Methane[b]
1	A	0.8	8	0.3	--	--	--	--	9	15
2	A	1.5	9	0.3	0.5	--	--	--	11	10
3	A	0.9	8	0.3	0.3	--	--	--	9	15
4	A	2	3	0.0	--	--	--	--	6	30
5	B	711	2175	425	375	120	250	75	4100	9000
6	A	--	3	--	--	--	--	--	3	5
7	B	247	122	--	3	3	--	--	375	3000
8	B	341	482	32	25	4	2	--	886	3000
9	A	2	6	1	1	--	--	--	10	10
10	A	--	4	--	--	--	--	--	4	2
11	B	59	129	3	--	--	--	--	191	500
12	A	---	5	--	--	--	--	--	5	10
13	A	--	12	--	--	--	--	--	12	25
14	B	800	3100	500	450	175	275	120	5420	9000
15	B	600	2300	300	220	120	180	90	3810	7000

a - A + Adequately designed multiple chamber incinerator; B = inadequately designed incinerator.

b - Infrared analysis.

TABLE II Gas Chromatographic Analysis of Some C_1 to C_5 Hydrocarbons Present in Incinerator Effluents

	Test No.				
	1	2	3	4	5
	Type of Incinerators[a]				
Compound	B	B	B	B	B
	Concentration, ppm				
Total C_2 compounds	3321	4400	3200	855	369
n-butane	35	70	20	---	---
i-butane	--	20	--	4	2
C_4H_3[b]	150	160	105	5	1
3 methyl butene	30	50	20	2	---
Pentene-1	25	40	12	---	---
n-pentane	48	85	30	---	---
2 methyl butene-2[c]	58	75	17	---	---
2 methyl pentane	56	77	50	---	---
3 methyl pentane	6	15	10	---	---
n-hexane	3	12	5	---	---

[a] B = inadequately designed incinerator.

[b] This peak includes: butene-1, isobutylene, butadiene 1,3, ethyl acetylene.

[c] This peak includes 2 methyl pentene-1.

The results indicate that, when the concentration of C_2 hydrocarbons is below 10 ppm, the C_2 to C_6 hydrocarbons are generally present in less than 1 to 2 ppm. When the C_2 hydrocarbons are present in high concentrations, the C_4 to C_6 compounds are generally present in significant concentrations. Some specific C_4 to C_6 compounds found in the effluents from incinerators have been identified.

The standard of 50 ppm of C_2 to C_6 hydrocarbons in incinerator effluents appears to be a satisfactory emission standard since it adequately differentiates between incinerators which are well designed and operated and those which are not.

Reference A-24 - 1960

This paper describes a continuation of the laboratory work described in reference A-25. Substantial variations in excess air, percent under- and over-fire air and refuse charge rate had little effect on total hydrocarbons. The following results were found:

	Hydrocarbon Content (ppm)	
	300% Excess Air	50% Excess Air
50% moisture fuel	26	45
25% moisture fuel	13	37

Reference A-25 - 1959

In a series of laboratory experiments carried out to evaluate the influence of incinerator design and operation on atmospheric pollution, hydrocarbon concentrations of the flue gases were monitored by a positive type infrared gas analyzer sensitized with hexane and operating at a wave length of 3.4μ with a range from 0 to 750 ppm (expressed as hexane). It is recognized that a hexane-sensitized instrument has zero sensitivity to acetylene and very low sensitivity to ethylene, acetone, benzene and other organic compounds which are normally encountered in incinerator flue gases. The system cannot reliably detect hydrocarbon concentrations of less than 30 ppm.

The findings relating to hydrocarbon and carbon monoxide concentrations can be applied to industrial and municipal incinerator design and operating practices. Since combustion at the 50% excess air level produced these contaminants, discharges are controllable by proper employment of combustion air as it relates to (1) distribution within the ignition chamber, and (2) levels of oxygen available in the combustion zone.

Tests were carried out on a multiple chamber experimental incinerator employing a uniformly prepared rubbish of 25% moisture content, which was burned under closely controlled conditions of charging and air distribution. Hydrocarbon production was intermittent, each occurrence lasting only one or two minutes depending on the combinations of conditions responsible for its productions. With 50% excess air, maximum concentrations ranged up to 400 ppm. With 150% excess air, there were no hydrocarbons in excess of the 30 ppm lower limit of detectability of the measuring system. The results of this work are given on the next page.

Fuel Burned	Air Distribution Under-fire	 Over-fire	Stack Discharge (scfm)	Hydro-carbons
50% Excess Air Level				
140	15	20	250	0.72
140	15	20	240	0.00
140	15	20	230	----
140	15	20	230	0.76
140	30	0	220	2.1
140	30	0	270	0.62
140	30	0	270	----
140	30	0	250	2.5
180	15	0	330	0.50
180	15	0	320	0.47
180	15	0	320	----
180	15	0	300	0.00
180	30	20	300	1.4
180	30	20	310	0.37
180	30	20	320	----
180	30	20	330	0.64
150% Excess Air Level				
140	15	0	400	----
140	15	0	390	0.00
140	15	0	380	0.00
140	15	0	440	0.00
140	30	20	400	0.00
140	30	20	370	0.00
140	30	20	350	0.00
140	30	20	370	0.00
180	15	20	490	0.00
180	15	20	480	0.00
180	15	20	510	0.00
180	15	20	490	0.00
180	30	0	500	0.00
180	30	0	530	0.00
180	30	0	490	0.00
180	30	0	450	0.00

2. Discussion

There is not very much information available in the literature concerning hydrocarbon emissions. Most of the work reported dates back eight years and longer. The hydrocarbon emissions appear to be quite low, generally being less than 1 lb/ton of refuse, and consequently have not been of much concern as a pollution hazard.

F. Specific Organics

1. Bibliography

Reference A-2 (1968)

In a summary of emission from municipal incinerators, the following emission levels are reported: aldehydes - 0.3 lbs/ton of refuse, organic acids (reported as acetic acid) - 0.6 lbs/ton of refuse.

Reference A-7 (1967)

In an evaluation of the specific organic compounds present in the stack effluent of incinerators, the results of a partial analysis of a representative sample (test run of sampling equipment) were:

33 g of water recovered from the 0°C traps contained about 10 ppm of both acetone and acetaldehyde, and methanol, ethanol, methylethyl ketone, a high molecular weight ketoalcohol, phenol, a high boiling hydrocarbon, a solid carboxylic acid salt (possibly a formate) and a solid high molecular weight alcohol, each of these in concentrations of about 1 ppm.

6.7 g of water collected in the trap cooled to -78°C contained concentration levels of about 1 ppm of methanol, ethanol, methylethyl (2) ketone, acetaldehyde, n-butyl alcohol and n-amyl alcohol; also a relatively higher concentration of acetone and less than 1 ppm of benzene.

Reference A-20 (1964)

In a program designed to characterize particulate emission from heat generation and incineration sources, the sampling system was specifically designed to trap polynuclear hydrocarbons by condensation and to minimize their loss when subjected to gas flow for extended periods of time. The sampling train includes ice bath water bubbles (32°F), freeze-out traps (-98°F) and a high efficiency fiber glass filter. The system was estimated to have removed 99% of the PNHs. After collecting total particulate weight, the benzene soluable fraction was analyzed by UV spectroscopy. The PNH species analyzed were in the range 0.01 to 2 μ grams per pound of refuse.

The initial step in determining polynuclear hydrocarbons involved benzene extraction of the particulate matter, the condensate, and the rinse liquids. Separation of the benzene-soluble fraction of the samples was done by column chromatography, and the analysis was made by ultraviolet visible spectrophotometry. The individual polynuclear compounds that were quantitatively analyzed include benzo(a) pyrene, anthracene, phenanthrene, pyrene, fluoranthene, benz(a) anthracene, benzo(e) pyrene, perylene, benzo(ghi) perylene, anthanthrene, and coronene.

These compounds can be placed in two groups corresponding to the relative reliability of the analytical determination for the individual compounds. Collection efficiency of the sampling train was 99% or better for all of the polynuclear compounds studied.

Benz(a) pyrene and benzo(e) pyrene were detected in the flue gases from every incinerator studied. The concentrations of pyrene from each unit were higher than those of any of the other polynuclear hydrocarbon compounds detected, and ratios of pyrene to benzo(a) pyrene ranged from 6 to 120. A summary of data measured for several incinerators is as follows:

POLYNUCLEAR HYDROCARBON EMISSION SUMMARY--INCINERATOR SOURCES[a]

	Municipal		Commercial	
	250-Ton/Day[b]	50-Ton/Day[c]	5.3 Ton/Day[d]	3 Ton/Day[d]
Benzo(a)pyrene	0.075	6.1	53	200
Pyrene	8.0	52	320	4200
Benzo(e)pyrene	0.34	12	45	260
Perylene			3.1	60
Benzo(g,h,i)perylene	34	0.63	90	870
Anthanthrene			6.6	79
Coronene	0.24	0.63	21	210
Anthracene			47	80
Phenanthrene		18	140	50
Fluoranthene	9.8	3.3	220	3900
Benz(a)anthracene	0.37	0.15	4.6	290

[a] A blank in the table for a particular compound indicates it was not detected in the sample.

[b] Breeching (before settling chamber)

[c] Breeching (before scrubber)

[d] Stack.

Reference A-22 (1962)

For comparison to experimental incinerator tests, a series of field tests were made on full-scale incinerators. Formaldehyde concentrations were measured by a technique involving the bubbling of a sample gas stream through chromatropic acid solution. Emissions from both the 50-ton and the 250-ton units were higher at the lower temperatures, and lower underfire air levels.

Summary of Average Emissions from 50-Ton/Day Batch Charge Furnace

Underfire Air, %	Excess Air %	Temp. Secondary Chamber (°F)	Formaldehyde[c]	
			1[a]	2[b]
20	235	1080	9.9×10^{-4}	7.2×10^{-4}
50	110	1500	2.2×10^{-4}	0.0×10^{-4}
70	100	1500	0.0×10^{-4}	0.0×10^{-4}

[a] From sampling point ahead of water spray scrubber.

[b] From sampling point after water spray scrubber.

[c] Lbs/1000 lbs dry flue gas (corrected to 50% excess air).

Summary of Average Emissions from 250-Ton/Day Continuous Feed Furnace

Combustion Conditions[a]		Temp. Sec. Chamber	Formaldehyde[b]
Underfire Air	Excess Air		
	190	1750	3.9×10^{-4}
50	180	1790	2.8×10^{-4}
80	190	1930	1.7×10^{-4}
100	150	1960	1.7×10^{-4}

[a] At sampling point in breeching.

[b] Lbs/1000 lbs dry flue gas (corrected to 50% excess air.

Reference A-30 (1962)

In this study, methods of sampling and analysis were those developed by the APC District of Los Angeles. The following table details emission findings.

Organic Emissions from Incinerators

Compound or Group	Emissions, lbs/Ton of Charged Material Single Chamber	Multiple Chamber
Methanol	9-23	.05
Ethylene	8-61	.05
Acetone	8	.05
Methane	23-150	.05
Acetylene	4-73	.05
Alpha Olefines (as propylene)	6	.05
Carbonyl Sulphide	3	.05
Benzone	3	.05
Acids (as acetic)	4	.05
Phenols (as phenols)	8	.05
Aldehydes (as formaldehyde)	5-64	.3
Ammonia	0.9-4	.05

Reference A-40 (1962)

A variation of the chromotropic acid method of formaldehyde analysis was investigated, which employs direct collection and color formation in a 0.1% chromotropic acid solution in concentrated sulfuric acid, instead of the usual method involving preliminary collection in a bubbler containing an aqueous bisulfite solution of just water. A brief study was also made of the use of an aqueous solution of chromotropic acid. The aqueous procedure is not useable in analyses of diesel or incinerator effluents; the acid procedure is not applicable to raw and diluted auto exhaust, but both can be used to analyze synthetic and actual photochemical smog. Because of its much higher sensitivity, the acid procedure is convenient for formaldehyde analysis, even when the formaldehyde levels are only a few parts per hundred million by volume. At these concentration levels and below, the use of optical cells of 5-cm path length are advisable. Thus, for trace gas analyses, direct collection in acid solution provides a more sensitive procedure than those various formaldehyde and aldehyde analytical methods that involve a 1-to-10 dilution step.

Reference A-18 (1957)

Samples for the determination of hydrocarbons and aldehydes are collected in evacuated bulbs. At least 4 samples are taken for each of the gases during a 1 hr test period. The bulbs for aldehyde samples contain sodium bisulfite absorbing solution. The aldehydes are determined by a modified Ripper's method, and are expressed as formaldehyde. The following emission levels (in lbs/ton of refuse) were given for two single chamber incinerators: organic acids (as acetic acid) - 2.0 and 3.9; aldehydes (as formaldehyde) - 0.03 and 2.7; hydrocarbons - nil; and acetylene - nil.

2. Discussion

As with total hydrocarbons, there is little literature data on the occurance and amounts of various organic species in incinerator emissions. Most reports lump all species of a functional group together. All aldehydes are reported as formaldehyde and all organic acids as acetic acid. As a result, the individual organic components have not been analysed in any detail. Detection procedures in the past have generally involved infrared spectroscopy. More recent studies combine gas chromatography and high resolution mass spectrometry.

G. Inorganic Acids

1. Bibliography

Reference A-34 (1968)

The maximum HCl content ranges around 0.02 vol. percent in wet flue gases. A municipal incinerator shows emissions of HCl from 0.122 to 0.204 grains/scf.

This study was done on European municipal incinerators. It states that the emission values for gaseous material depend practically exclusively upon the refuse composition, the proportion of plastics and industrial refuse. No information was given about sampling or analysis methodology.

2. Discussion

There is essentially no data given on inorganic emissions. The increased usage of chlorinated and fluorinated plastics as packaging materials has caused some concern about future increases in HCl and HF emissions. The employment of appropriate APC methods can probably keep inorganic acid emissions to very low levels.

H. Volatile Metals

1. Bibliography

Reference A-27 (1953)

Emission spectrographic analysis of material collected in a precipitator thimble (representing 77 percent of total particulate) yielded less than one percent lead and zinc.

2. Discussion

There are no reports in the literature of specific attempts to measure levels of volatilized metals. It is expected that low melting point metals that are present in the refuse such as lead and tin will volitilized and/or condensed metals will undoubtedly be emitted to the atmosphere. Present sampling and analysis techniques are not suitable for quantifying these emissions.

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APPENDIX B THE NATURE OF THE INCINERATOR PROCESS

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APPENDIX B

THE NATURE OF THE INCINERATOR PROCESS

I. INTRODUCTION

The purpose of operating an incinerator is to reduce the volume of solid waste materials; converting the combustible matter to gaseous products while producing a minimum of residual solid ash. Because of the moment-to-moment variability of materials that are fed into an incinerator, the accomplishment of this objective is a difficult task.

The processes involved in the operation of a municipal incinerator are: accumulation of the refuse in a storage area or pit; feeding the refuse to the furnace; burning; cleaning the flue gases of particulate collection and removal of residue; and discharge of the gaseous effluents. Those systems with a system for air pollution control will also have a need for a separate system handling the collected solids. Effective emission testing of an incinerator requires an understanding of these variabilities and that they can affect the outcome of the test.

This chapter will discuss types of waste encountered, the various types of incinerators and the incineration processes which are currently being used. A more in-depth discussion (from which almost all of the material was taken) can be found in a three-volume report to NAPCA (now EPA) under Contract CPA-22-69-23 by Arthur D. Little, Inc., entitled: "Systems Study of Air Pollution from Municipal Incineration.[4] The following chapters of that report are particularly pertinent to this report, Volume I, Chapter V, "The Nature and Causes of Air Pollution," Sections A and B, and Appendix H, "The Incinerator Process."

II. THE SOLID WASTE PROBLEM

The increasing quantity of collected municipal solid waste, coupled with changes in the refuse itself--composition, heating value, ash content, and the like--point to the need for new or expanded incineration facilities for the future and for new plant designs and standards to preclude air pollution problems. Table B-1 presents an analysis of the national annual average composition of municipal refuse in 1968.[4] These estimates were computed from data from 23 sources, modified to provide an average composition of municipal waste. These averages can only be considered estimates of the composition of average national refuse because of the limited quantity of data available. Also, some variations can be expected, reflecting localized mixes of commercial and domestic waste sources, industrial wastes, and so forth. The differences between geographical locations can be seen from the data in Table B-2.

Table B-3 presents an ultimate analysis of refuse categories by oxidizable elements and inerts.

TABLE B-1

Average Refuse Composition - As-Discarded Basis*

Category	Wt (%)	Description
Glass	8.3	Bottles (primarily)
Metal	8.2	Cans, Wire, Foil
Paper	35.6	Various Types, Some with Fillers Polyvinyl Chloride, Polyethylene, Styrene, etc., as Found in Packaging, Housewares, Furniture, Toys and Nonwoven Synthetics
Leather & Rubber	1.5	Shoes, Tires, Toys, etc.
Textiles	1.9	Cellulosic, Protein, and Woven Synthetics
Wood	2.5	Wooden Packaging, Furniture, Logs, Twigs
Food Wastes	23.7	Garbage
Miscellaneous	1.7	Inorganic Ash, Stones, Dust
Yard Wastes	15.5	Grass, Brush, Shrub Trimmings
	100.0%	

*Taken from Reference 4, Vol. I, page IV-16.

TABLE B-2

Estimated Annual Average of Municipal Refuse Composition (1968)*
("As-Discarded" Basis)

Category	Un-Seasonal State (e.g., Florida)	Semi-Seasonal State (e.g., Alabama)	Seasonal State (e.g., Massachusetts)
Glass	7.6	8.1	8.8
Metal	7.5	8.1	8.7
Paper	32.6	35.1	28.2
Plastics	1.0	1.1	1.1
Leather & Rubber	1.3	1.4	1.5
Textiles	1.8	1.9	2.0
Wood	2.3	2.4	2.7
Food Wastes	18.2	19.5	21.1
Yard Wastes	26.1	20.7	14.1
Miscellaneous	1.6	1.7	1.8

*Taken from Reference 4, Vol. I, page IV-15.

TABLE B-3

Estimate of the National Annual Average Composition of Municipal Refuse Excluding Yard Wastes and Miscellaneous Categories[+]

(as-fired basis)

(1) Component	(2) Data[*] Samples Utilized	(3) Mean Weight Percent	(4) % Mean (100% basis)	(5) Estimated Standard Deviation S(X)	(6) 95% Confidence Limits	(7) 95% Confidence Range
Glass	23	9.7	9.9	4.37	1.89	8.0-11.8
Metal	23	10.0	10.2	2.18	.93	9.3-11.1
Paper	23	50.3	51.6	11.67	5.04	46.6-56.6
Plastics	9	1.4	1.4	.96	.74	0.7-2.1
Leather & Rubber	9	1.9	1.9	1.62	1.25	0.7-3.2
Textiles	17	2.6	2.7	1.80	.93	1.8-3.6
Wood	22	2.9	3.0	2.39	1.06	1.9-4.1
Food Wastes	23	18.8	19.3	10.95	4.73	14.6-24.0
		97.6				

[+] Taken from reference 4, Vol. I, p. IV-10

[*] Several data sets were not presented in a form suitable for extracting the weight fractions of all of the above refuse components.

The anticipated changes in the nature of this refuse over the next 30 years are particularly significant. Over this time span, study data point to a more than 70% increase in the per capita refuse generation rate over the current level which, when compounded by the effect of increasing population, will increase by a factor of 2.65 the quantity of generated solid waste. Thus, a community with a stable population level may well experience a refuse disposal requirement increase of 70% and an area growing in population at the national average rate will require an incineration capacity over 2.5 times that in 1968 by the year 2000.

In order to project the per capita waste loads and refuse composition for each state, national indicators were developed for each of the 10 major categories comprising municipal refuse. These indicators reflect the national growth rates (through the year 2000) in the production of the commodities comprising the major (but not necessarily all) sources of each refuse component. The indicator for plastics, as an example, was developed from weighted averages of the consumption projections for plastics used in packaging, housewares, furniture, toys, and synthetic-nonwoven textiles. These are major sources of plastics in municipal wastes. Projections of the consumption of these segments of the plastics market should, therefore, provide a realistic tool for estimating the growth of plastics in municipal refuse.

It should be noted that there are varying "lag times" between the purchase and disposal of the various components of refuse. These lag times have been estimated and incorporated into the development of these national indicators for categories which are changing rapidly. Plastics packaging, for example, has substantially no lag time associated with its disposal. Plastics in furniture, however, may have lag times varying from a few years to 30 years or longer, depending on the type of furniture and its use. An average lag time of 10 years was estimated for plastics in furniture.

These indicators are not in themselves national projections of the quantities of the various components contained in the national refuse. Each indicator merely projects the national growth rates of materials and goods comprising that classification of refuse with appropriate adjustments for lag time between consumption and disposal.

The projected national annual growth rates of each of the 10 major refuse components as obtained from the indicator projections are shown in Table B-4. For some components, such as food wastes, rubber and leather, and wood, the annual growth rate is predicted to remain relatively constant. The annual growth rate of plastics, metal, and glass are predicted to vary considerably. Plastics, for example, are predicted to have significant growth rates through 1980, but then to level off at a relatively stable growth rate of about 5% per year.

TABLE B-4

Average Annual Refuse Category Indicator Growth Rates (g'_i)*

Time Period		Paper Products (%)	Miscellaneous & Food Wastes (%)	Metal (%)	Glass (%)	Plastics (%)	Textiles (%)	Rubber & Leather (%)	Wood (%)	Yard Wastes (%)
From	To									
1968	1970	4.5	1.1	4.0	5.4	11.9	4.1	3.2	1.0	2.6
1970	1970	4.5	1.1	4.0	5.4	11.9	4.1	3.2	1.0	2.6
1975	1980	3.6	1.1	3.9	3.9	11.4	3.6	3.2	0.9	2.6
1980	1985	3.7	1.8	2.8	2.6	5.6	4.6	3.3	1.1	2.6
1985	1990	4.2	1.6	2.7	2.1	5.6	4.7	3.3	1.0	2.6
1990	1995	3.9	1.5	1.5	1.7	5.0	4.4	3.7	0.8	2.6
1995	2000	4.0	1.4	0.4	0.8	4.7	3.9	3.7	0.9	2.6

*Taken from Reference 4, Vol. I, page IV-19.

III. INCINERATORS

This discussion is presented in order to provide the reader with some idea of the engineering aspects of incinerators. A more comprehensive discussion can be found in Appendices H and I of Reference 4.

Figure B-1 shows the annual incinerator construction over the past 30 years. It can be seen that the majority of the plants now operating in this country were built in the late 1950's and the early 1960's.

A. Types of Incineration

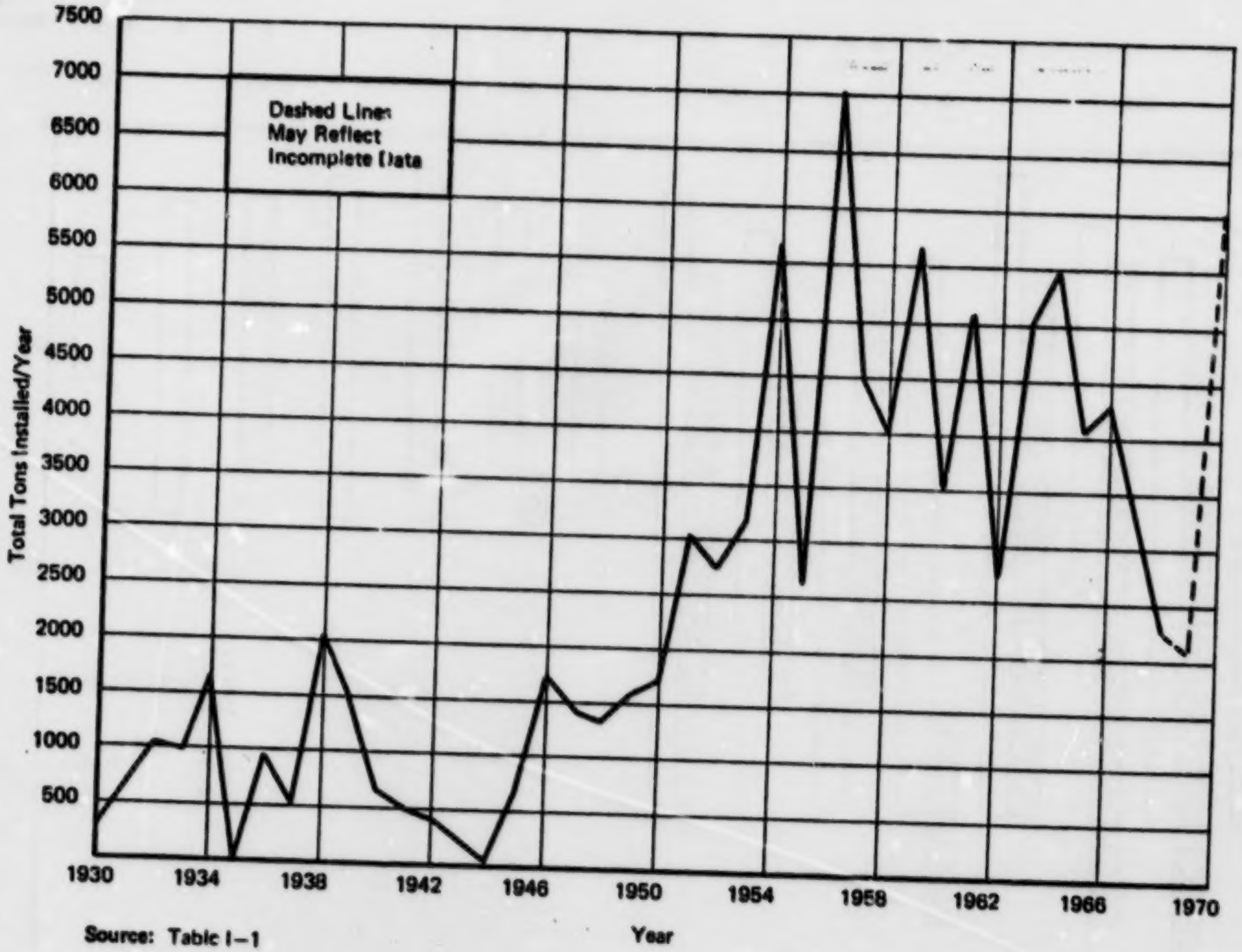
Incinerators fall into two major classifications--batch feed and continuous feed. Batch feeding of refuse can be done directly into the furnace manually, or with a clamshell bucket or grapple attached to a travelling crane; the rate of feed is controlled by the time cycle and the degree of bucket loading. In a few plants, a front-end loader operating on a paved floor charges the furnace; sometimes with a ram. One of the main characteristics of a batch feed unit is that it operates in cycles--adding refuse and burning (perhaps several times) and then dumping the grate--so that each step of the operation recurs on a periodic basis. As may be anticipated, a larger level of emissions from batch incinerators occurs during or immediately following the charging or dumping steps (as compared to "normal burning").

Within the continuous feed category, there are a large number of concepts--but most are comprised of refractory chambers of rectangular construction. A few units use a kiln following combustion on a grate to improve burn-out and a very small number (in the U.S.) use waterwall boiler construction (grate burning) followed by a convection boiler.

Most recent construction specifies continuous feeding of refuse to the incineration furnace. Continuous feeding is most often accomplished by means of a hopper and a gravity chute. A rectangular hopper receives the refuse delivered by the crane and bucket. The bottom of the hopper terminates in a rectangular section chute leading downward to the furnace grate or other feeder conveyor at the entrance to the furnace chamber itself.

Intermittent feeding of refuse directly into the furnace is done, in most cases, with a clamshell bucket or grapple attached to a traveling crane.

Figure B-2 presents a picture of the change in type of furnace from batch to continuous as well as an indication of the furnace capacity. In regards to the latter point, it should be recognized that an incinerator facility frequently will have two or three furnaces so that incinerator capacity varies from less than 100 tons per day (TPD) up to 1200 TPD.



Source: Table I-1

FIGURE B-1: Total Annual Additions to United States Incinerator Capacity (See Table I-1, Vol. 1)*

*Taken from Reference 4, Vol. II, page I-26.

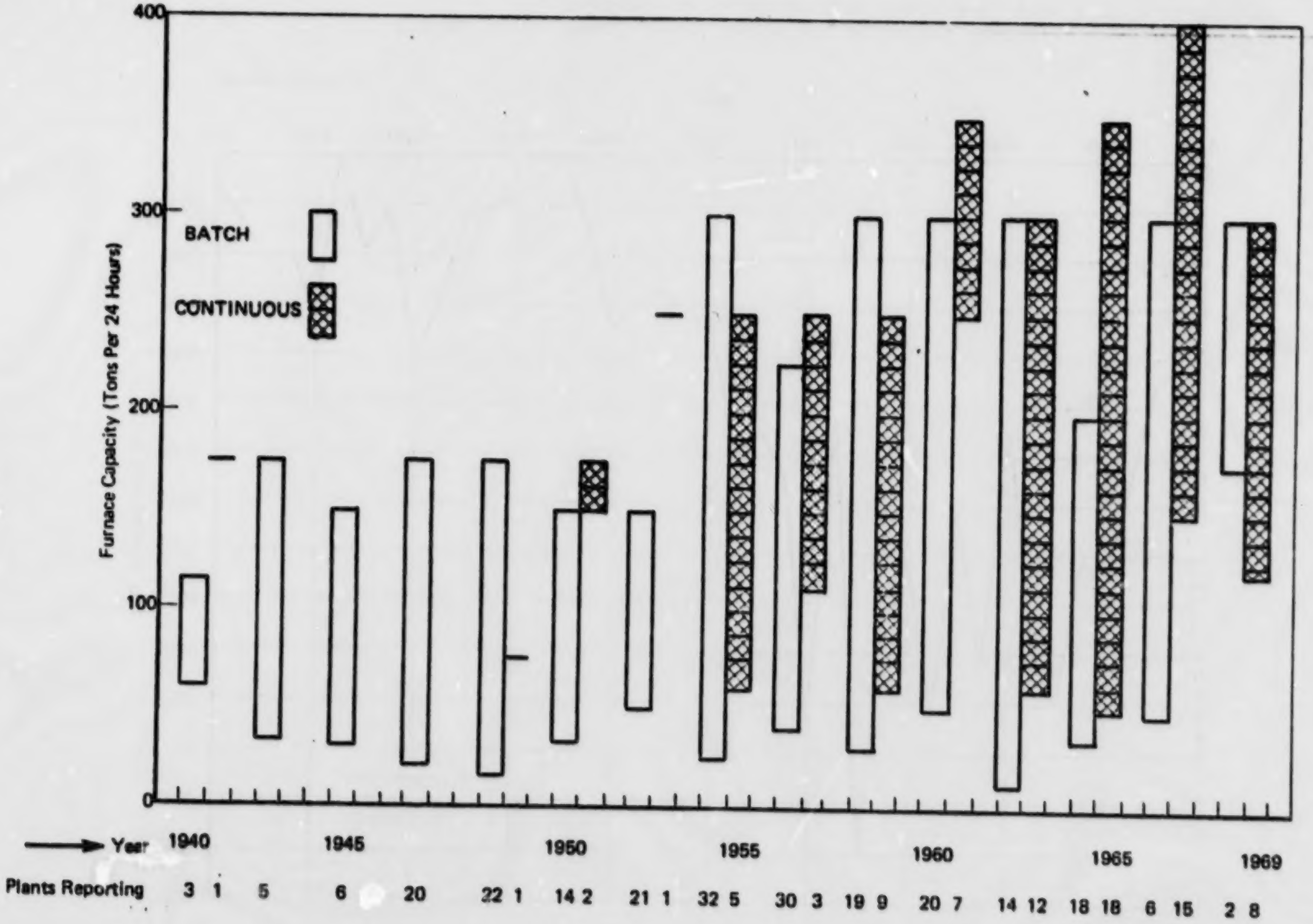


FIGURE B-2: Range of Furnace Capacities Batch and Continuous*

*Taken from Reference 4, Vol. II, p. I-32.

B. Important Operation Factors

1. Grates and Hearths

Nearly all incinerator furnaces employ either a stationary refractory hearth to support the burning refuse or a variety of grate types which stoke or mix the refuse during the combustion process in various ways depending upon the type of grate or stoker. Suspension burning (not now used in municipal incineration practice) would be the only process which does not necessarily require a hearth or grate, since most of the refuse would be oxidized while in suspension in furnace gases. To obtain acceptable burn-out with suspension burning, a burn-out grate should be provided at the bottom of the furnace chamber.

There are many different types of hearth or grate, each of which has its own special features.

a. Rotary Kiln, Stationary Hearth, and Rotary Hearth

Incinerator furnace systems which operate without grates include the stationary hearth, rotary hearth, and rotary kiln. The stationary hearth is usually a refractory floor to the furnace. The rotary hearth, which is seldom used for refuse, involves a rotating refractory table that turns on a vertical shaft by means of a mechanical device operated from below.

The rotary kiln type of hearth has been used for several hundred years in the pyroprocessing industry to move solids in and out of high-temperature combustion zones and to mix them during combustion by rotating them. The kiln is inclined toward the discharge end and the movement of the solids being processed is controlled by the speed of rotation. There has been no use of the rotary kiln for municipal incinerator furnaces except after the burning of refuse on a multiple-grate system.

b. Grates

- Stationary Grates

Stationary grates are metal bars or rails supported in the masonry side walls of the furnace chamber. They normally require manual stoking with a slice bar to stir the burning bed of refuse in order to obtain reasonably complete combustion. This grate system is now found only in very old or very small incinerators.

- Mechanical Grates

Mechanical grates are grates that are activated periodically to mix the burning refuse and dump the ash. Mechanical grates are being used in many of the newer batch fed incinerators. The grate moves the refuse and residue from the refuse feed point through the incinerator furnace to the discharge end of the grate, and does some stoking and mixing of the burning materials on the grates.

c. Stokers

Incinerator stokers are mechanical devices to burn solid refuse. They provide support and continuous or intermittent conveying of the refuse bed (sometimes with stoking), often are supplied with most of air for combustion, and act to discharge the non-combustible residue from the furnace. Thus, the stoker is not only a conveyor, but a means to control the combustion process. In fact, the incinerator stoker is the principal item for control in the incinerator furnace system. It establishes or affects the rate of refuse feed (in the continuous flow system), the rate of combustion, the residence time of the refuse in the combustion chamber, the completeness of the combustion or burn-out, the temperature of the combustion chamber, and the temperature of the ash residue discharged from the system.

2. Furnace Enclosures

The furnace enclosure provides a controlled environment for the combustion process in the incinerator system. Without the furnace enclosure, the combustion process would, in effect, be "open burning." Materials for conventional incinerator furnace enclosures include:

- Nonmetals (refractories, i.e., firebrick walls and roofs);
- Metal (plate, tubes, pipe, etc.);
- Refractory covered metal (castable or firebrick refractory lining or coating, 1" to 9" thick).

There are at least three types of refractory enclosures: gravity walls with sprung arch roofs; suspended walls and suspended roofs; and refractory linings supported directly by a metal shell.

Either water or air may be used to cool these enclosure materials. Cooling water can be either contained in tubes or pipes or uncontained in the form of a film on the surface of the external metal plate. Air cooling can be employed with forced convection; with forced air jets impinging on the surface; or by radiation and natural convection to the ambient environment. Warmed cooling air can be used as preheated air for combustion or can be ducted for building heat.

The use of waterwall enclosures is of increasing interest. These enclosures are characterized as waterwall boilers or waterwall incinerator furnaces. Such walls are cooled by forced circulation of hot water or by natural convection as in steam boiler tubes.

The physical shape of the furnace enclosure is a factor in controlling the incineration process. For example, there is a tendency for hot combustion gases to rise to the top of the chamber. If the furnace outlet is at the top of the enclosure, the cooler gases from the discharge portion of the grate will leave the furnace below the layer of hotter combustion gases, often without mixing. Thus, a large fraction of the combustion air is not used and the flue gases may contain excess air as well as unburned combustible. This problem is reduced somewhat with chamber designs which exhaust the gases from the incinerator furnace either at the top near the refuse feed or at the lower portions of the furnace near the ash discharge. The installation of overfire air jets, refractory baffles, or bridge walls will also aid mixing.

3. Combustion Air

For incineration, the term combustion air usually includes underfire air, overfire air, and secondary air. Underfire air is required to cool the grates (to maintain their structural integrity and to avoid oxidation corrosion of the grate metal), and to furnish oxygen for the combustion reaction. It may be insufficient for complete combustion, yet sufficient to release enough heat to pyrolyze the refuse and remove the volatile components. Although it is common practice to pass a quantity of underfire air theoretically sufficient for complete combustion of the refuse on the grates, poor air distribution vis-a-vis the distribution of air demand, and poor gas mixing requires additional air as overfire or secondary air for mixing and for dilution of the gases to maintain temperatures below 1800°F to 2000°F, respectively.

Overfire air is usually admitted either in low- or high-velocity jets to mix the combustible gases rising from the burning refuse with combustion air. Secondary air, added for temperature control, may be admitted through high-velocity jets in the side walls and roof of the furnace enclosure, either near the upstream end of the primary furnace or at the transition between the primary and secondary furnace. Also, secondary air can be added at low velocity through a slot or small openings in the bridge wall separating the primary chamber from the secondary chamber. In the latter case, mixing is dependent more on the shape of the chamber and changes in direction of the main gas stream, than on the energy carried by the air jets.

4. Flue Gas Conditioning

Inasmuch as the incineration of municipal refuse is a combustion process, it is necessary to remove the heat that is generated. In the past, this has usually been done with a gravity stack which, except for the heat lost through the incinerator walls, discharged most of the combustion energy to the atmosphere as sensible heat in the hot flue gases. The heat of evaporation of moisture in the refuse and from cooling of flue gases by water sprays is discharged as latent heat of the water vapor in the flue gases.

However, cooling of the flue gases to carbon steel operating temperatures (below 600°F to 700°F) as may be necessary for several APC or stack systems, is frequently required. It can be accomplished by one or a combination of any of three methods:

- By direct injection and vaporization of water;
- With a heat exchanger, such as a waterwall or convection boiler, air-cooled refractory, or an air preheater; and
- By dilution and mixing with cool atmospheric air.

5. Air Pollution Control

The emission of mineral particulates is controlled most effectively by incineration Air Pollution Control (APC) systems which are the only means of reducing stack concentrations of noncombustible gaseous pollutants. APC devices are selected on the basis of a compromise between the initial capital investment required, the cost of operation, and the desired efficiency of collection. Operating characteristics, reliability, and water pollution potential usually play lesser roles in the selection procedure.

Settling chambers are the simplest, least expensive, and least effective of the APC systems now used to remove particulate pollutants. Basically, this chamber slows the flue gases (no temperature reduction necessary) to permit gravity settling of the coarse particulate. The calculated performance of a "perfect" settling chamber (nominal dust size and density, 30 feet high, and a 5-second residence time), is about 40%; realistically it would probably be closer to 20%.[9]

Other devices used to collect particulate emissions include mechanical collectors, such as cyclone devices, fabric filters, and electrostatic precipitators which separate the dust particles from the effluent by interaction of electrical charges placed upon the surface of the dust particles. The latter is capable of very high collection efficiencies. Fabric filters, properly designed and operated, promise to be more effective in the removal of particulate matter than any of the conventional APC systems. The particulate collection efficiency of these devices often exceeds 99%. Also, some absorption of HCl may take place on the alkaline fly ash material in the dust cake. By 1968, however, no filter units have been installed in U.S. incinerators.

Various types of scrubbing devices are currently used for contacting liquids with gas streams to remove particulate matter and gaseous pollutants. These include wetted surfaces, liquid sprays, and bubbling gas devices. The wetted surface and liquid spray devices are more prominently used in municipal incinerators. However, all such devices are noted for their side effects in humidifying and cooling the gas, thus producing a steam plume at the stack under certain atmospheric conditions.

In general, gaseous pollutants will pass unchanged through the dry control devices, except the bag filters which have purportedly absorbed as much as 90% of the H_2SO_4 values[3] but little of the SO_2.[6] Wet control devices, although primarily used as particulate removal agents, will remove some of the gaseous pollutants. However, most wet scrubber devices are less effective than a single-equilibrium contact. Analyses have shown that particulate scrubbers can be expected to remove--in addition to material particulates--a portion of the H_2SO_4, HCl, SO_2, organic acids, and in some cases CO_2. Other components--CO, NO, hydrocarbons, aldehydes, and SO_3--are essentially untouched except by scrubbing.

Figure B-3 shows the shifts in the choice of primary air pollution control equipment among incineration plants. The primary incineration control equipment is that having the greatest effectiveness. In many plants, a combination of sprays and wet-bottom expansion chambers are used, followed by a higher efficiency system, such as close-spaced wetted baffles, or a high-energy scrubber. There is a distinct trend away from the dry expansion chamber systems (and "none") toward increased use of cyclones, close-spaced wetted baffles, and scrubbers.

Modification of certain factors in the incineration process may alleviate air pollution somewhat, for instance, the shift toward continuous units and closing of older batch units. The batch units have considerably higher combustible pollutant loadings, though total particulate emissions tend to be slightly lower than the continuous plants. The charging operation is related to air pollution and a number of other operating problems associated with batch fed units. Figure B-4 shows, as a histogram for cylindrical and rectangular units, the various responses from operators to questions regarding charging frequencies. Although the responses were widely variable, they appear to concentrate in the range of 5-10 charges per hour.

Data on charging and dumping frequency for batch-feed units and on the residence time for continuous-feed traveling grate units are summarized in Table B-5. It can be seen that the batch-feed units require a considerably longer grate residence time than continuous-feed units.

Table B-6 shows reported values for flue gas temperatures in various parts of the furnaces, according to furnace type. Although some variability is shown, the reported values are quite similar. In all cases, the temperatures shown are more than needed to assure complete burnout of all combustible air pollutants. The fact that such materials do appear at substantial concentrations in stack effluents indicates the unreliability of the reported measurements as representative averages. It is clear, from other data,[13] that stratification occurs in furnaces, permitting substantial amounts of colder gas to pass through the system.

The range of gas temperatures that can be expected in a stack on a municipal incinerator without wet scrubbers is shown in Figure B-5. Clearly, in some cases the gas stream that must be sampled is still quite hot.

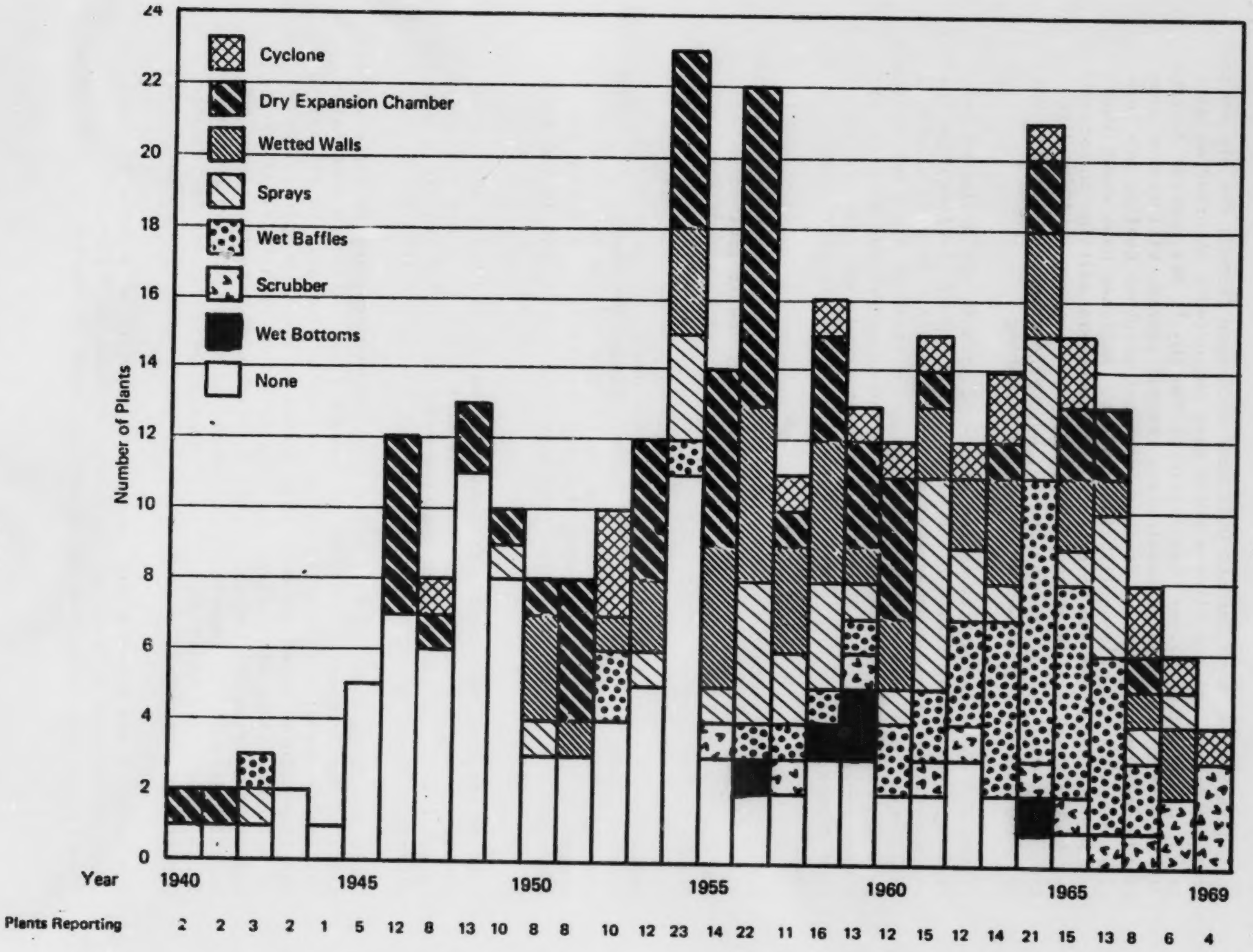


FIGURE B-3: Primary Air Pollution Control Equipment*

*Taken from Reference 4, Vol, II, page I-34.

TABLE 5

Average Grate Residence Time

Furnace Type	Average Grate Residence Time (min.)
Circular Batch	116
Rectangular Batch	103
Traveling Grate	61
Hearth (manual Stoked)	180
All Types	94

TABLE 6

Reported Incinerator Temperatures

	Furnace Type					
	All Units	Grate-Kiln	Circ. Batch	Rect. Batch	Continuous	Hearth
I. Primary Chamber Average Temp (°F)	1675	1833	1581	1621	1725	1850
II. Secondary Chamber Average Temp (°F)	1288					
III. Stack Average Temp (°F)	636					

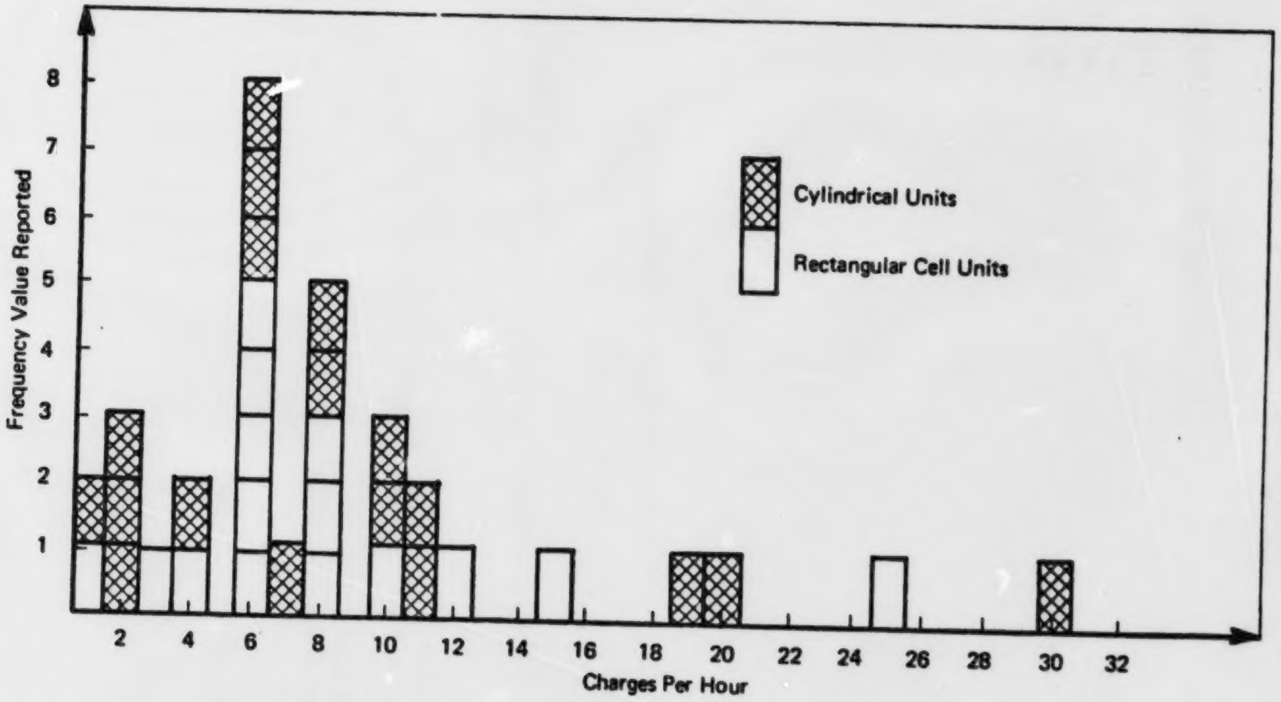


FIGURE B-4: Frequency of Occurrence of Charging Rates, Batch Feed Incineration Systems*

*Taken from Reference 4, Vol, II, page I-50.

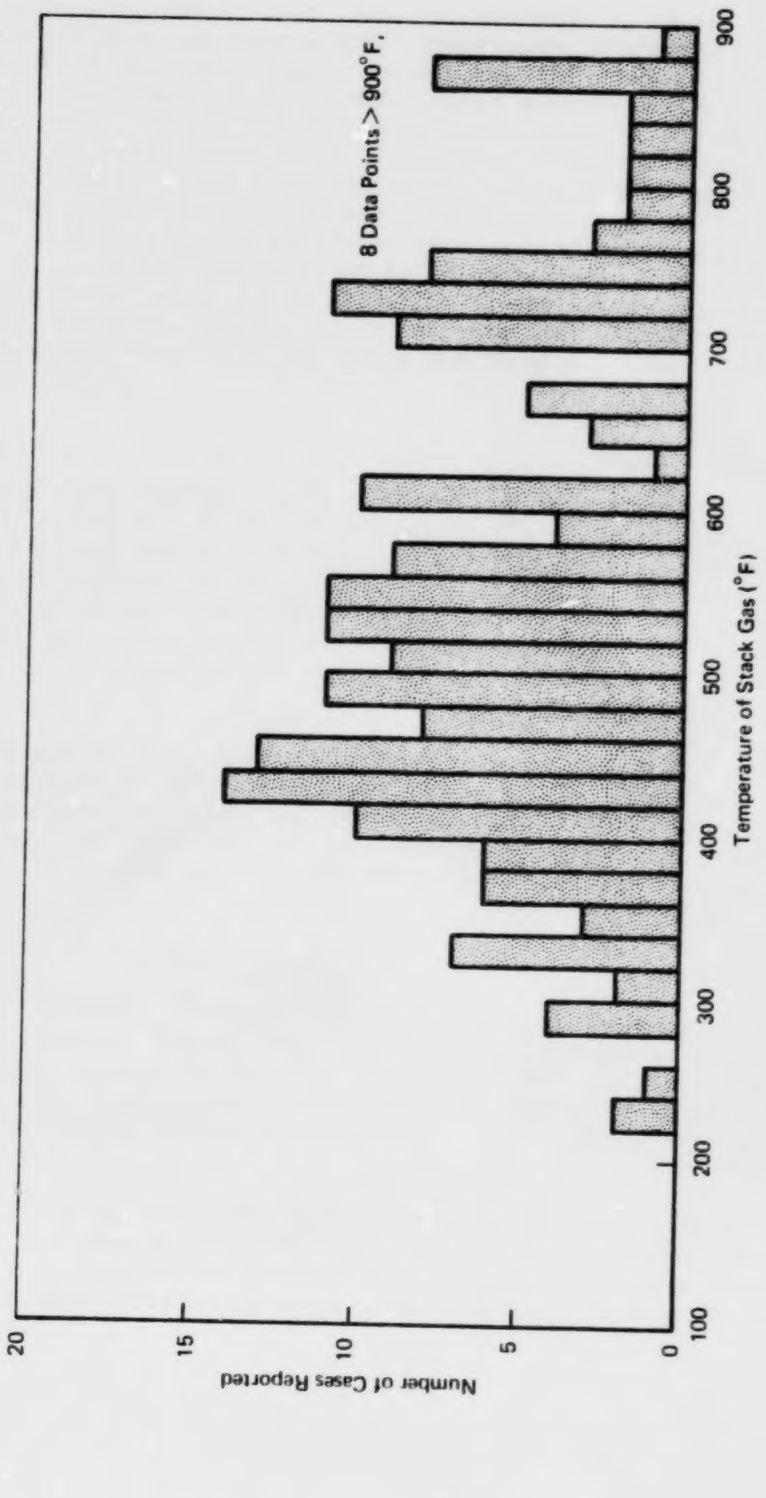


FIGURE B–5 HISTOGRAM OF AVERAGE GAS TEMPERATURES IN STACK FOR MUNICIPAL INCINERATORS
(Based on Data from Appendix J, Reference 4)

6. Stacks

Several types of stacks or chimneys are used to discharge incinerator flue gases into the ambient atmosphere. Stub stacks are usually fabricated of steel and extend a minimum distance upward from the discharge of an induced draft fan. Stacks taller than about 5 diameters and less than 100 feet high are often referred to as "short" stacks. These are either constructed of unlined or refractory lined steel plate, or are constructed entirely of refractory and structural brick. "Tall" stacks are constructed of the same materials as the short stacks above, and are used to provide greater draft than that resulting from the shorter stack, and to obtain more effective diffusion of the flue gas effluent. Some metal stacks are made with a double wall with an air space between the metal sheets. This double wall provides an insulating air pocket to prevent condensation on the inside of the stack and thus avoid corrosion of the metal.

7. Ash Removal

After complete incineration of the refuse, the ash residue drops into an ash chamber or chute from the end of the grate or kiln. Siftings that have fallen through the grates (which may have been either partially or completely oxidized) and collected fly ash also may be conveyed to this ash chamber. The ash may be discharged directly into a container or onto suitable conveyors for disposal, or into water for quenching and cooling. The ash residue is then removed from the water with a drag conveyor, pusher conveyor, or other means.

To prevent inleakage of air or outleakage of furnace gases at the point where the gas is removed, an air seal is desirable. Dry mechanical seals and seals made by covering the ash receptacle or container have been used to control air leakage. With wet removal of the ash, a wet or hydraulic (water) seal is utilized or a combination of a wet and mechanical seal is used (Martin ash quencher seal).

IV. GASEOUS EMISSIONS

If combustion of the volatile fraction of the refuse is complete, the composition of the flue gas will be principally nitrogen, oxygen, and carbon dioxide. There will be small amounts of sulfur oxides, nitrogen oxides, and traces of mineral acids (principally hydrochloric acid, which will result from the combustion of halogenated plastics, particularly polyvinyl chloride).

If combustion of the volatiles is not complete, the flue gases will contain significant amounts of carbon monoxide and other uncombusted or partly combusted organic materials. A more detailed description of the composition of the effluent gas stream is given in Appendix A of this report.

V. PARTICULATE EMISSIONS FROM INCINERATORS

An appreciation for the factors that determine particulate emission and for their relative importance may be gained by considering the three mechanisms mainly responsible for the emissions:

- The mechanical entrainment of particles from the burning refuse bed;
- The cracking of pyrolysis gases; and
- The volatilization of metallic salts or oxides.

The first of these mechanisms is favored by refuse with a high percentage of small particle size, low density ash, by residue or residue geometry favoring entrainment (plates), by high underfire air velocities, or by other factors that induce a high gas velocity through the bed. The second mechanism is favored by refuse with a high volatile content producing pyrolysis gases with a high carbon content and by conditions above the fuel bed that prevent the burnout of the coked particles formed by the cracking of the volatiles. The third mechanism is favored by high concentration of metals that form low melting point oxides and by high temperatures within the bed.

Furnace emissions depend on many variables: refuse composition; method and frequency of feeding; underfire air; incinerator size; burning rate and temperature; combustion chamber design; grate type; and mixing.

A. Refuse Composition

Ash particles may be entrained when the velocity of the gases through the fuel bed exceed the terminal velocity of the particles. Undergrate air velocities typically vary from a minimum of 10 SCFM/ sq. ft. of grate area to 100 SCFM/sq. ft. Based on the terminal velocity of ash particles, it is expected that particles up to 70 μ (equivalent diameter) will be entrained at the lowest velocities and up to 400 μ at the highest.

The large volumes of combustible-rich pyrolysis gases generated during the incineration of refuse with a high volatile content tend to result in particulates with a high fraction of soot and other combustibles. Sooting tendencies are particularly high for pyrolysis gases with a high carbon content.

B. Method and Frequency of Feeding

Start-up of an incinerator is a time when particulate emissions are generally high. Therefore, a batch process, by definition, will have a cyclic pattern with high emissions at the start of each cycle. The amount of emissions will be highly dependent on the charge and manner of feeding. The behavior of continuous systems also can be greatly influenced by the rate of feeding of the refuse.

C. Underfire Air Rate

A systematic study of the PHS[11] of the effects of underfire air, secondary air, excess air, charging rate, stoking interval, and fuel moisture content on the emission rate from an experimental incinerator led to the conclusion that the velocity of the underfire air was the variable that most strongly influenced particulate emission rate. The wide variations in undergrate air use between different incinerators partially accounts for the scatter seen in collections of particulate emission data. Unfortunately, however, such engineering data are seldom measured or reported during emission testing.

D. Incinerator Size

Increasing the size of incinerator units from 3 to over 100 TPD (tons per day) has been shown to result in higher emission rates, but the effect of size on emission factors has not been quantitatively established over the more limited size range of municipal furnace units (50-300 TPD). Part of the increase is due to the higher burning rates (lb/hr-sq ft of grate), and hence higher underfire air rates associated with large units.

E. Burning Rate

It is expected that higher emission rates will be encountered at higher burning rates. Rhem[2] cites that reductions in rate of burning to 70% of rated capacity have shown as much as 30% reduction in furnace emission from that at full capacity; however, insufficient data are available for a quantitative relationship to be established as important variable changes specified.

F. Combustion Chamber Design

Practically the only data in this area are provided by the studies on small incinerators in Los Angeles County. From these data, it was concluded[7] that the emission from small units could be reduced substantially by the use of multiple chambers and by the use of a low arch. The emission in these tests primarily consisted of particles under 5 μ in size, and there is uncertainty concerning the applicability of the results or the design parameters developed to large municipal incinerators. The need for multiple combustion chambers for large units, for example, will depend mainly on the adequacy of mixing in the primary chamber.

G. Grate Type

Although the type of grate used in an incinerator does not in itself define the emission rate of pollutants, it can be viewed as an integral variable reflecting the effect of a number of parameters, including: specific undergrate air flows, the stoking intensity, and the percent open air.

H. Mixing Effects on Combustible Pollutants

The reduction in combustible solid and gaseous pollutants within an incinerator is primarily a function of the mixing processes within the system. In all realistic cases, the bulk flue gas temperature and the calculated average gas residence time within the furnace are more than adequate to assure complete combustion. Therefore, insufficient mixing plays an important role in generation of particulates.

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Proc. 1968 National Incinerator Conference, New York, May 5-8, 1968, p. 142-53.

APPENDIX C EVALUATION OF EXISTING SAMPLING TRAINS

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APPENDIX C

EVALUATION OF EXISTING SAMPLING TRAINS

I. INTRODUCTION

This appendix presents a discussion of the methodology currently in use for sampling incinerators for particulates. In evaluating these methods, it is important to recognize that particulate matter, as considered by EPA for our study, was any material, except uncombined water, which would be in the solid or liquid state at 70°F and a pressure of one atmosphere. To be effective and useful as a monitoring method, applicable procedures and devices should remove a measured representative sample of stack gas, collect the particulate matter (solid and liquid) which exists in the stack gas, as well as the potential particulate matter, i.e., material which would condense to an aerosol (free liquid water excepted) as incinerator gases cool by dilution with the ambient atmosphere. The ultimate method should make possible the collection of particulate and potential particulate matter without the introduction of any extraneous material which could be misinterpreted.

In addition to focusing attention on the mass of emitted particulate matter as a measure of its effect as a pollutant, currently there is interest in many other effects of air pollution, such as: cloud formation in the atmosphere and its relation to nuclei population; influence on atmospheric visibility and haze by small particulates (0.1 to 1μm); health effects of the "respirable" fraction (approximately 0.1 to 5μm); and the mass of material emitted to the atmosphere in the larger size range (>1μm).

All particulate sampling systems include the following units:

- nozzle
- probe
- collecting device
- metering unit
- suction source

These units are not always independent components of the system, for example, a cyclone is sometimes used for particle collecting and gas metering. The design of the sampling system, both as to configuration and size, may be dependent on the sampling procedure contemplated and the interests of the designer. In any case, the arrangement of the components, both as to location and sequence, is a primary feature in differentiating systems.

II. DESCRIPTION AND EVALUATION OF EXISTING SAMPLING SYSTEMS

Six systems were selected as being significant and state of the art in their arrangement and/or application. These have been associated with the following groups:

- Environmental Protection Agency - EPA (formerly PHS);
- Los Angeles Air Pollution Control District (Los Angeles APCD);
- Incinerator Institute of America, Procedure T-6;
- An ASME PTC Type System;
- British Standards System; and
- WP-50 System.

A. EPA System

The description of the EPA (formerly PHS) sampling system specified for testing incinerators is presented as Appendix K in this report.

The most widely leveled criticism of this system has been directed toward the nature of the material caught after the filter. In a series of incinerator studies using this system, it was found that the weight of the material collected after the filter varied from a few percent to 75% of the total sample weight with an average of 30%.(1) In view of the low reproducibility of the impinger catch, suspicion abounded that some of the material found in the impinger train was produced by chemical action in the aqueous scrubbing solution, hence was not particulate matter under the definition of particles as utilized for our investigation. Also, since the impinger train was in an ice bath (32°F), material may have been formed physically (condensation) which was not consistent with the present definition of particulate (particles which exist at 70°F).

Another potential problem with this system has been the use of a heated glass probe in place of an all metal probe. By supporting the glass probe in stainless steel, it is hoped to take advantage of the fact that glass is less reactive chemically (except for HF) compared to metal. Hopefully, continued field experience with the glass system will reduce the problem of potential breakage to an acceptable level.

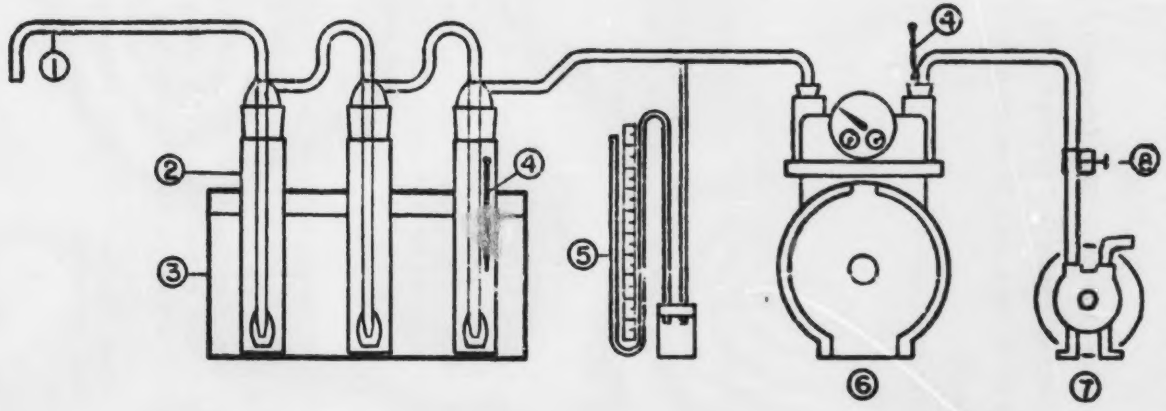
Finally, it should be noted that the earlier PHS system included the impinger catch as part of total particulate whereas the procedure described in Appendix K does not.

B. Los Angeles APCD Type System

The Los Angeles system(2) shown in Figure C-1, is similar to the EPA system and appears to be an earlier version of it. However, this system is significantly different from the EPA system in that the materials of

FIGURE C-1

Los Angeles APCD Type System*



Schematic diagram of sampling train incorporating a miniature glass cyclone, alundum thimble filter, and impingers. This equipment is frequently used when sampling incinerator effluent, where particles larger than 5 microns are common. The components are: (1) sampling probe; (2) cyclone; (3) electric heaters; (4) dry filter; (5) impinger (dust concentration sampler); (6) ice bath container; (7) thermometers; (8) mercury manometer; (9) hose clamp; (10) vacuum pump; and (11) Sprague dry gas meter.

*Taken from Reference 2.

construction are not as well chosen from a chemical reactivity point of view, i.e., stainless steel probe and filter holder plus rubber or tygon tubing connections. These features could tend to decrease the accuracy of this system.

Another Los Angeles APCD system(2) functions similarly to the one in Figure C-1 except that a filter downstream of the impingers is used to capture particles which pass through the impingers. It is reported that the filter collects a very small amount of material compared to the impingers, but this would be expected since it collects only particles which pass through the impingers plus carry-over from the impingers. Backing up the impingers with a filter is a prudent technique in that it prevents accumulation of carry-over in the sample lines and it protects the pump and metering system from possible contamination. However, it could lead to early filter plugging and necessitate shortened sampling times.

C. Incinerator Institute of America, Procedure T-6

IIA Procedure T-6(3) is designed for large volume sampling (>5 cfm) of dust (solid particles $\gtrsim 1 \mu m$); therefore, as a system it only partially fulfills the particle sampling requirement under the EPA definition. The apparatus consists of a 3/4-inch diameter null (balance) nozzle, a stainless steel probe with one section water-cooled (to protect the filter downstream from the hot sample gas). The probe attaches to a well-packaged stainless steel cyclone (mason jar pot) and low efficiency bag filter. The pump is a large volume centrifugal type. This system is shown in Figure C-2.

While the null nozzle allows rapid flow adjustment, it has small static pressure ports which are subject to plugging. Also, a sensitive differential pressure gauge (such as Hooke gauge) is necessary to determine the null point. The most positive feature of this system is that the collection stage (made by UOP Air Correction) is packaged in a convenient package for field handling. The significant negative features are:

- Materials of construction (large opportunity for reaction with the sample gas);
- Difficulty in recovering all the sample from the collection stage; and
- No direct sample gas volume measurement.

D. An ASME PTC Type System

The American Society of Mechanical Engineers performance test codes (PTC 21-1941 and PTC 27-1957)(4) do not specify particular equipment, but they do outline the basic requirements for a sampling system.

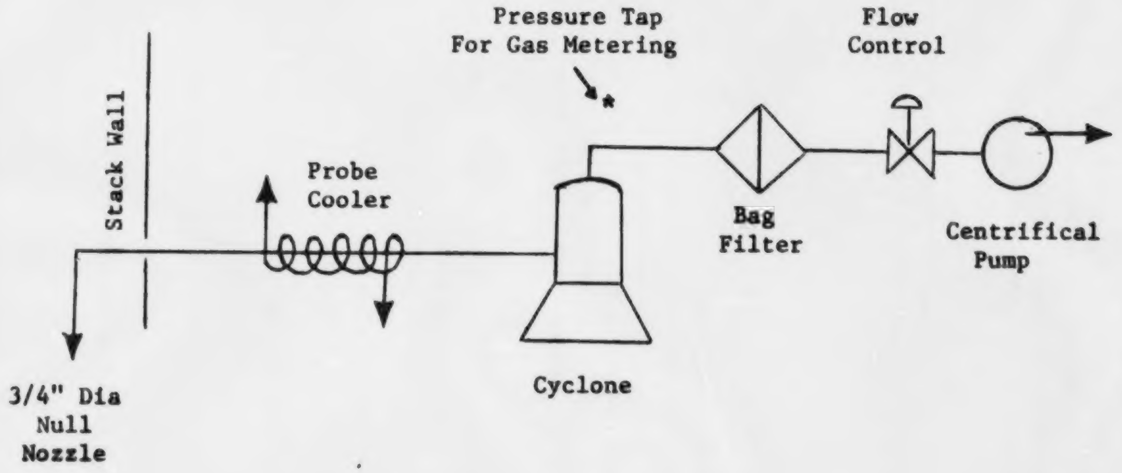

Pressure Tap
For Gas Metering
*
Flow
Control
Stack Wall
Probe
Cooler
Bag
Filter
Centrifical
Pump
3/4" Dia
Null
Nozzle
Cyclone

FIGURE C-2

Schematic of T-6 System

The comments on the IIA/T-6 system apply here with the exception that this system does not appear to be as convenient to use because of its increased bulk and overall poor packaging. In spite of these apparent difficulties, many people feel that the system is reliable and easy to use in the field.

E. British Standard System

This system$^{(5)}$ was developed by the British Coal Utilization Research Association for sampling stack gas from coal-fired power plants. Since then, the system has been established as a British Standard and used for general particle source testing in the United Kingdom and Commonwealth countries. The apparatus consists of a nozzle leading directly to a cyclone (used for sample gas flow measurement) which is closely coupled to a packed glass filter. All of this equipment is located inside the stack. A centrifugal pump outside the stack is used for suction. Stainless steel is the construction material throughout.

This system is designed for large volume sampling of dust; therefore, as a system it only partially meets the requirements for particle sampling under the EPA definition. (Large volume flow systems must sacrifice in filter efficiency to avoid rapid plugging.) However, this system has features that are worth discussing. The location of the collection stages inside the stack reduces the effort in recovering sample material from probes. It eliminates the need for an external heating source to maintain the cyclone and filter above the dewpoint (hot stack gases). This equipment appears to be convenient to transport, to set up, to operate, and to recover the sample. In operation, it is simple to adjust the flow for isokinetic conditions since the flow meter (cyclone) operates at the same gas temperature and pressure condition as a pitot tube located close to the nozzle. Since both the pitot tube and the flow meter are square law devices, a simple linear calibration curve may be drawn for a given size nozzle that relates ΔP across the meter to ΔP across the pitot tube. The relationship is independent of the stack conditions. This curve allows an operator to quickly and accurately adjust the flow to isokinetic conditions.

F. WP-50 System

The WP-50 system$^{(6)}$ is widely used in stack sampling and is shown schematically in Figure C-3. In the conventional form, this system consists of a buttom-hook-type nozzle connected directly to an alundum thimble filter holder, all of which are located inside the stack. The filtered sample gas is then drawn through a pipe (and frequently moisture condenser) to a dry gas meter and a sunction source. The construction material is stainless steel.

This system is designed for measuring dust, hence, only partially fulfills the requirement for particle sampling under the EPA definition. The following positive features are noted about this system: sample easily recovered (short sample line to collector; and total sample gas volume measures.

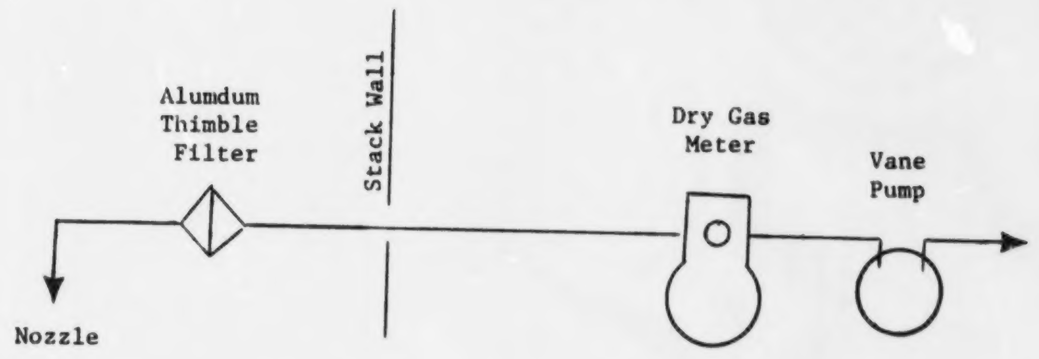

Alumdum
Thimble
Filter
Stack Wall
Dry Gas
Meter
Vane
Pump
Nozzle

FIGURE C-3

WP-50 System

The potential negative features are: filter (thimble) plugging especially in saturated gas stream; no monitor of flow rate for quick isokinetic adjustment; reactive construction materials; and because of large weight of thimble, large sampling volumes are required in order to collect sufficient sample to overcome large tar weight of the filter.

There are two types of systems specified by the Industrial Gas Cleaning Institute for wet scrubber testing (inlet and outlet) which are modifications of the WP-50 system, hence, most of the above discussion applies. The significant modification to the outlet system is an electrically heated filter thimble which reduced filter plugging due to condensed water. The modification to the inlet system seems regressive in that a calibrated orifice has been substituted for the dry gas meter.

III. DISCUSSION

Some general observations which are appropriate to this overall presentation are given below.

There is a wide variety of sampling systems reported in the literature from which the above six systems have been selected and discussed individually. While they are all different in detail, they include the following features:

- intake nozzle
- sample collection stage(s)
- sample gas metering stage(s)
- pump (includes any aspiration technique

Furthermore, they fall into only four general arrangements as shown in Figure C-4. All systems in use today fit into the types of Figures C-4a, b, c. It is difficult to conceive of a system of the type in Figure C-4d, where all the collected sample could be recovered. A system of this type is depicted in the ASME PTC 21 and 27 but no actual device of this type is known to be in use today.

The components which comprise the features of a sampling system are based on what is to be measured plus features the designer deems a convenience. The systems which have been examined have been designed for the following criteria:

(a) sample for solid particulate $\gtrsim 1 \mu m$ using large volume sampling ($\sim$1.5 to 20 cfm);

(b) sample for solid particulate $\gtrsim 1 \mu m$ using small volume sampling ($\sim$.5 to 1.5 cfm);

(c) sample for particles and condensible vapors using small volume sampling.

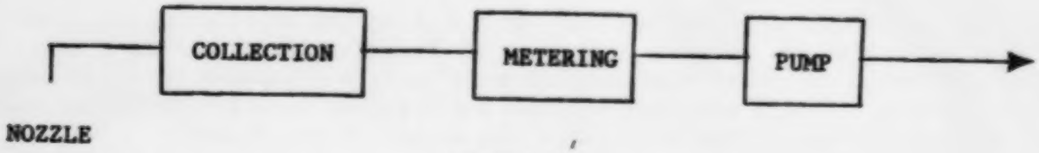

COLLECTION
METERING
PUMP
NOZZLE

FIGURE C-4a

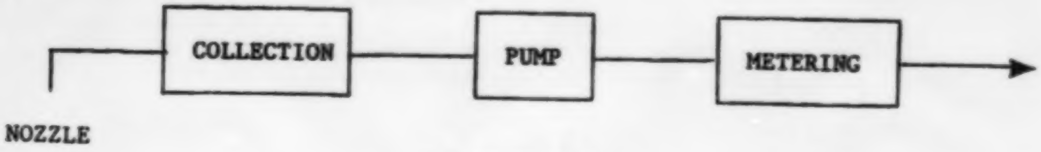

COLLECTION
PUMP
METERING
NOZZLE

FIGURE C-4b

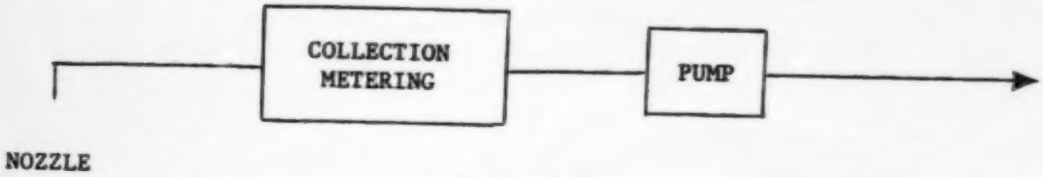

COLLECTION
METERING
PUMP
NOZZLE

FIGURE C-4c

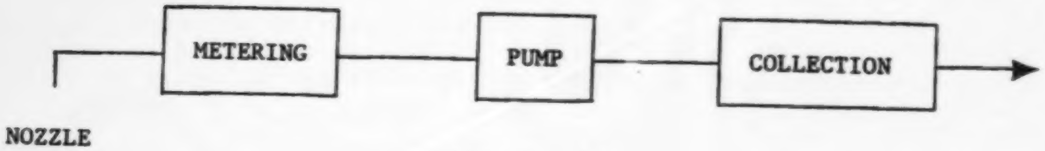

METERING
PUMP
COLLECTION
NOZZLE

FIGURE C-4d

FIGURE C-4

Generalized Sampling Systems Configuration

With the equipment designed for criteria (a), non-solid matter is ignored and the gas metering system is designed for large flow rates (usually a calibrated orifice or a cyclone). The flow rate must be accurately recorded as a function of time to obtain the volume of gas sampled. The pump must be a high volume type such as centrifugal blower or large ejector. The equipment designed for (b) has a collection stage similar to (a) but smaller in size, the gas metering may be the orifice/cyclone technique (for flow rate monitoring) and/or a dry gas meter for sample volume. The pump is usually a mechanical vane vacuum pump ($\gtrsim$20" Hg static). The equipment designed for (c) is similar to (b) but has a collection stage for condensible vapors, i.e., cooled Greenberg-Smith impingers, and filter selection is very critical.

Sample methodology for particulate source sampling is undergoing change. The modern definitions of particulate make different demands on sampling apparatus and techniques than the traditional definition. Presently, the best attempt to satisfy these new demands is the EPA system.

The EPA system is certainly not the definitive answer to modern, incinerator, particulate source sampling; however, it does have the following positive features:

- Consideration of collecting total particulate; and
- A system design concept.

With the exception of the Los Angeles system, none of the other systems evaluated attempted to collect condensible vapors; in fact, most of these systems were not designed to collect particles less than one micrometer. None of the other systems showed overall engineering design. Most sampling systems have the appearance of being assembled and not designed. The EPA system has obviously been designed. Some consideration has been given to the chemical reactivities of the construction materials and packaging for ease of operation and installation. However, it is not clear that this system is able to measure particulate matter under the EPA definition.

The most significant questions to be resolved about the EPA and other like systems are:

- Is any material being formed in the collecting system? When the impinger residue is included in the particulate weight, there has been an opportunity for chemical reaction in the impinger to form solids after collection. Therefore, this could be considered false particulate and lead to measurement errors.

- Is there an inconsistency between the measurement method and the desired definition of particulate when the sample is cooled to ice bath temperature, returned to room temperature and weighed?

The pretreatment of impinger residue prior to weighing calls for extraction, evaporation under heat, and drying via desiccation. Such a complicated procedure is subject to many potential errors.

Particulate matter present in the stack can be collected at high efficiency with many of the present sampling systems as is or with appropriate modification. However, the present methods advocated for the collection of condensibles can not be expected to determine quantitatively the condensibles which would form in the atmosphere since the conditions are so different. In fact, to simulate the atmospheric composition, temperature, relative humidity and radiation in a sampling system is unreasonable. Therefore, measurement of total particulate matter which includes condensibles should be interpreted as "potential" total particulate.

This review of the present state of the art and the instrumentation used in incinerator sampling has indicated to us that alternate and more sophisticated means of collecting and evaluating condensible material merits further study.

IV. REFERENCES

1. AN EVALUATION OF SEVEN INCINERATORS
W. C. Achinger and L.E. Daniels
Proceedings of the National Incinerator Conference (1970), p. 32-61.

2. SOURCE TESTING MANUAL
Air Pollution Control District, Los Angeles County, Los Angeles (1963).

3. INCINERATOR TESTING
Bulletin T-6, Incinerator Institute of America, New York, New York (August, 1968).

4. DETERMINING DUST CONCENTRATIONS IN GAS STREAMS--Performance Test Codes, PTC 27-1957, The American Society of Mechanical Engineers.

5. SIMPLIFIED METHOD FOR MEASUREMENT OF GRIT AND DUST EMISSIONS FROM CHIMNEYS
British Standards Institution, London, B.S. 3405 (1961).

6. BULLETIN WP-50
Western Precipitation Division, Joy Manufacturing Company, Los Angeles, California.

APPENDIX D

TABULATION OF SAMPLING RUNS

A complete list of all sampling runs conducted under this program is given in the following tables. These tables are grouped by the objective of the runs rather than sequentially by date of sampling. The relation of the objective of the sampling runs to the remainder of this report is indicated below. Even though all of the runs did not generate samples which were used for detailed characterization, the total series is tabulated for reference purposes. Also, material collected during individual sampling runs sometimes were used for several purposes, so that data collected during the experimental program from that run may be reported in more than one place.

Table No.	Objective of Sampling Run	Discussion of Data Main Report Section No.	Discussion of Data Appendix
D-1	Become familiar with EPA sampling train and collection of samples for general use	4	E
D-2,3	Study filter efficiency under freed conditions and collection of samples for general use	--	E,G
D-4	Evaluation of a commercial sampling train under field conditions and collection of samples for general use	3	E,F
D-5	Examination of filter catch directly on the filter using x-ray, optical, and scanning electron microscopy, and collection of samples for general use	--	E,H
D-6,7	Collection of samples for chemical characterization and quantitative analysis	4	F

Table D-1

EPA System Familiarization Experiments

Run No.	Date	Filter Type	Dry Gas Volume (m^3)	Sampling Time (min.)	Stack Temp. (°F)	Filter Temp. (°F)	Impinger Outlet Temp. (°F)	Filter Weight Gain (mg)
NI-1	4/8/71	Glass	1.44	60				191
NI-2	4/14	"	1.15	40				336
NI-3	4/15	"	1.69	64				174
NI-4	4/15	"	2.04	80				391
NI-5	4/20	"	1.61	60				283
NI-6	4/21	"	2.24	80	260-280	260-280	70-100	
NI-7	4/21	"	1.46	60	320-280	280	77-84	
NI-8	4/22	"	1.62	60	300-380	280	75-130	
NI-9	4/22	"	1.65	60	380-400	280	75-80	263
NI-10	4/22	"	1.67	60	380-400	280	84-102	359

Table D-2

Filter Leakage Experiments

Run No.	Date	Filter Type	Dry Gas Volume (m^3)	Sampling Time (min.)	Stack Temp. (°F)	Filter Temp. (°F)	Impinger Outlet Temp. (°F)
NI-11	4/27/71	Glass	1.65	60	280-335	280	77-110
NI-11A		"	2.78	60	300-335	285-295	--
-12		"	1.50	60	320-360	280	90-105
-12A		"	2.65	60	320-360	280-320	--
-13	5/4/71	"	0.91	60	320	280	65
-13A		"	0.86	60	320	270-280	--
-14		"	0.89	60	340-355	280	65
-14A		"	0.86	60	340-355	270-280	--
-31	6/18/72	"	0.82	60	240-340	260-290	95
-31A		"	0.82	60	260-340	280-320	--
-32		"	0.84	60	320-360	260-290	85
-32A		"	0.88	60	320-360	240-270	--

Table D-3

Filter Leakage Experiments

Run No.	Date	Filter Type	Dry Gas Volume (m³)	Sampling Time (min.)	Stack Temp. (°F)	Filter Temp. (°F)	Impinger Outlet Temp. (°F)
Test 1							
NI-15	5/17/71	Glass	0.91	60	300-340	280-320	70-75
NI-15A		"	0.85	60	300-340	260-280	---
NI-16		"	5.55	240	300-340	350-330	65-90
NI-17		"	0.91	60	320	250	65-70
NI-17A		"	0.85	60	320	250	---
Test 2							
NI-18	5/7/71	"	0.90	60	300	250-270	65-70
NI-18A		"	0.83	60	300	250-290	---
NI-19		"	2.45	90	300-330	240-260	85-90
Test 3							
NI-20	5/13/71	"	0.91	60	260-280	250-270	60-65
NI-20A		"	0.86	60	260-280	220-270	---
NI-21		"	3.43	180	270-300	250-290	---
Test 4							
NI-22	5/18/71	"	0.85	60	280	250-260	65
NI-22A		"	0.83	60	280	230-265	---
NI-23		"	4.27	175	220-310	240-280	65-80
NI-24		"	0.88	60	280-310	250-260	75
NI-24A		"	1.02	60	280-310	240-260	---
Test 5							
NI-25	5/19/71	"	0.85	60	300-340	240-270	65-70
NI-25A		"	0.89	60	320-340	260-290	---
NI-26		"	3.44	180	300-340	265-275	75
NI-27		"	0.44	45	280-380	270-290	270
NI-27A		"	0.80	45	280-320	260-290	---

Table D-3

Filter Leakage Experiments (Continued)

Run No.	Date	Filter Type	Dry Gas Volume (m^3)	Sampling Time (min.)	Stack Temp. (°F)	Filter Temp. (°F)	Impinger Outlet Temp. (°F)
Test 6							
NI-33	6/22/71	Glass	0.87	60	300-380	260-290	75
NI-33A		"	0.84	60	300-380	260-290	---
NI-34		"	3.03	180	300-380	260-290	70-80
NI-35		"	0.86	60	380-440	260-280	80
NI-35A		"	0.90	60	380-400	260-280	---
Test 7							
NI-36	6/23/72	"	0.84	60	320-350	270-275	65
NI-36A		"	0.93	60	320-350	380-390	---
NI-37		"	3.87	150	300-380	270-290	75-80
NI-38		"	0.84	60	350-360	280-290	75
NI-38A		"	1.03	60	350-380	270-300	---

Table D-4

Sampling System Evaluation Tests

No.	Date	Dry Gas Volume (meter^3)	Sampling Time (min.)	Average Stack Temp. (°F)	Outlet Temp. (°F)	Filter Weight Gain (g)
NI-39	7-7	1.69	65	270	95	--
-40		1.69	65	310	85	--
-41		1.58	87	330	95	989*
-42	7-15	2.35	96	250	85	563
-43		2.55	105	285	85	551
-44	7-22	2.47	100	300	85	--
-45		1.49	60	330	80	271
-46		2.13	93	400	75	563

*This weight includes the filter catch from runs 39, 40 and 41.

Table D-5

Filter Catch Samples
Collected for Examination Via Microscopy

No.	Collection Media*	Weight of Catch	Sampling Time	Purpose
NI-47	Organic Membrane	8.6 mg	---	X-Ray Analysis
-48	" "	4.0	---	"
-49	" "	7.0	---	"
-50	Silver Membrane	**	5 sec	Optical Microscopy
-51	" "	**	10 sec	"
-52	" "	**	5 min	"
-53	Organic Membrane	0.1	10 sec	"
-54	" "	32.6	+	Wet Chemical Analysis
-55	" "	31.6	+	"
-56	" "	32.7	+	"
-57	" "	59.7	+	"
-58	" "	2.0	5 sec	Optical Microscopy
-59	" "	---	7 sec	"
-60	" "	1.6	15 sec	"
-61	" "	1.1	22 sec	"
-62	Silver Membrane	**	5 min	"

* Organic Membrane - esters of cellulose, Millipore, SSWP04700 (3μm pore size).
Silver Membrane - Flotronics, MF-47-5 (5μm pore size).

** Silver membrane filters were not tared.

+ Sampling was continued until pump pressure reached 20" Hg.

Table D-6

Samples Collected for Quantitative Analysis

Run No.	Date	Dry Gas Volume	Sampling Time	Average Stack Temp.	Average Outlet Temp.	Filter Weight Gain
Continuous Grate Incinerator						
NI-69A	9/23/71	0.17	11	>310	---	---
-69B		0.06	4	>310	---	---
-69C		0.08	8	>310	---	---
-69D		0.25	22	>310	---	---
Batch Incinerator						
BI-70	8/31/71	1.28	70	460	90	278
-71	9/14/71	1.46	70	390	70	168
-72		1.50	70	395	75	191
-73	9/16/71	1.50	70	405	75	200
-74		1.44	60	425	85	293
-75	9/21/71	1.42	70	390	75	197
-76		1.71	80	410	80	248

Table D-7

Samples Collected for Chemical Characterization

No.	Date	Filter* Type	Dry Gas Volume (m^3)	Sampling Time (min.)	Stack Temp. (°F)	Filter Temp. (°F)	Impinger Outlet Temp. (°F)	Filter Weight Gain (mg)
NI-77	10/14/71	Membrane	0.57	33	320-450	195-205	60-70	50
NI-78		Glass	0.59	28	400-720	230-295	60-80	153
NI-79		Membrane	0.53	44	620-700	190-210	60-75	124
NI-80		Glass	0.59	32	425-710	245-300	60-70	108
BI-81	11/9/71	Membrane	0.56	15	280-350	210	<50	31
BI-82		Membrane	0.57	28	360-420	180-210	<50	44
BI-83		Glass	0.57	27	420-460	180-240	<50-60	74
BI-84		Glass	0.67	29	360-420	215-240	50	103
NI-85	12/8/71	Glass	1.34	60	425-485	220-248	50-120	377
NI-86		Glass	1.37	60	400-425	210-250	50-70	232
NI-87		Glass	1.27	60	410-430	200-240	50-65	261
NI-88		Glass	1.53	60	420-430	210-270	60-75	269

*Membrane - Millipore SSWP 3μ.
Glass - 1106 BH.

APPENDIX E

QUALITATIVE CHARACTERIZATION OF PARTICULATE CATCH

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APPENDIX E

QUALITATIVE CHARACTERIZATION OF PARTICULATE CATCH

A major focus of this program has been the development of a characterization approach which will generate useful and meaningful data about the character and composition of the particulate catch. A wide variety of chemical and physical techniques were explored to learn whether they could be of assistance in this task. Figure 2 in the main report (reproduced as Figure E-1 here) provides an overview of these techniques. In this appendix, a discussion is provided on the qualitative character for each portion of the particulate catch. The results of our quantitative studies to determine elemental composition is given in Appendix F.

I. FILTER CATCH

Although a few studies were made on the probe washings, most of our qualitative studies of the mineral particulate was done on samples of filter catch, therefore, this section covers results associated with both types of particulate catch.

A. Elemental Analysis

Using x-ray fluorescence (XRF) and emission spectroscopic techniques, the "classical" particulate catch was examined in an effort to learn the identity of the components of that catch. The results of these studies whereby the sample was collected on glass fiber filters is shown in Tables E-1 and E-2.

The x-ray fluorescence and emission spectrographic methods are complimentary and yield good agreement for the major elemental species. The particulate that collects in the nozzle, probe and cyclone has essentially the same chemistry as the filter particulate.

Relative Concentration Levels	Element
High	Pb,Zn,Cl,Si,Ca
Medium	Sn,K,S,Pb
Low	Br,Cd,Cu,Fe

Al,Mg and Na are not detectable by the XRF method employed, but emission spectrographic analysis has shown the presence of these three elements.

TABLE E-1

Results of X-Ray Fluorescence Analysis

(S - Strong; M - Medium; W - Weak)

Run No.	Br	Ca	Cd	Cl	Cu	Fe	K	Mo	Pb	S	Si	Sn	Sr	Ti	Zn
A. NI-3-1 - Filter and Loose Particles															
1	--	M	W	S	--	--	M	--	M	M	W	M	--	--	S
2	M	W	W	S	--	W	M	--	S	M	W	M	--	--	S
3	W	M	--	S	--	W	M	--	S	M	W	M	--	--	M
4	W	M	W	S	W	W	M	--	S	M	W	W	W	W	S
9	--	M	W	S	W	--	M	--	S	M	W	M	--	--	S
10	--	M	W	S	W	--	M	--	S	M	W	W	--	--	S
Ave.	W	M	W	S	W	W	M	--	S	M	W	M	--	--	S
B. NI-3-2 - Acetone Washings from Probe, Nozzle and Cyclone															
1	W	S	W	M	W	W	M	W	S	W	W	M	W	M	S
2	W	S	W	M	W	W	W	W	S	W	W	M	W	M	S
3	M	S	W	S	W	W	W	--	S	W	W	M	W	M	S
4	W	S	W	S	W	W	M	W	S	W	W	W	W	W	S
9	W	S	W	M	--	W	W	--	S	M	W	W	M	M	M
10	W	S	W	M	--	W	W	--	S	W	W	W	W	W	S
Ave.	W	S	W	M	W	W	W	W	S	W	W	W	W	M	S
C. NI-3-3 - Impingers (Water Residue)															
1	W	W	--	--	--	--	W	--	--	S	--	--	--	--	W
2	M	W	--	W	W	--	W	--	--	M	--	--	--	--	W
3	M	W	--	M	--	--	W	--	W	S	--	--	--	--	M
9	W	W	--	--	--	--	W	--	--	S	--	--	--	--	W
10	M	M	--	--	--	--	W	--	W	S	--	--	--	--	W
Ave	M	W	--	W	--	--	W	--	--	S	--	--	--	--	W

TABLE E-2

Results of Qualitative Emissions Spectrographic Analysis

Percent * Present	Sample Type and Number		
	Filter (NI-3-1)	Probe Washings (NI-3-2)	Impinger Residue (NI-3-3)
10 - 100	--	Ca	--
3 - 30	Ca,Si	Si	Al
1 - 10	Zn,Na	Fe,K,Ti,Na,Zn	B,Ca
0.3 - 3	Al,Pb,Ti	Al,Mg,Pb	Cr,Si,Na
0.1 - 1	Fe,K,Mg,P	P	Zn
0.03 - 3	Ag,B,Cu,Cr,Sb,Sn	Ag,Ba,Cu,Cr,Ni,Sn,Sb	Fe,Ni,Pb
0.01 - 0.1	Cd,Mn	B,Cd,Mn	Cu,K,Mn,Sn,Ti
0.003 - 0.03	Ba,Ni	Sr	Ag,Ba,Cd
0.001 - 0.01	Mo	Co,Mo	--
0.0003 - 0.003	Ga,Sr	Ga,V	--
0.0001 - 0.001	Ge	Ge	--
	NI 10-1	NI 10-2	NI 10-3
10 - 100	--	Si,Ca	--
3 - 30	Ca,Si,Zn	--	Al
1 - 10	Na,Ti,K	Fe,K,Ti,Na,Zn	B,Ca
0.3 - 3	Fe,Pb	Al,Mg,Pb	Cr,Si,Na
0.1 - 1	Al,Mg,P,Sb,Sn,Cu	P	Zn
0.03 - 0.3	Ag,Cr,Cd	Ag,Ba,Cu,Cr,Ni,Sb	Fe,Ni,Pb,Sn
0.01 - 0.1	B,Mn	B,Cd,Mn,Sn	Cu,K,Mn,Ti
0.003 - 0.03	Ba,Ni	Sr	Ag,Ba,Cd
0.001 - 0.01	Mo	Co,Mo	--
0.0003 - 0.003	Ga,Sr	Ga,V	--
0.0001 - 0.001	Ge,Be	Ge,Be	--

*All elements below the .03-3 range should be considered as minor constituents.

Unfortunately, although more field engineering studies have been done with glass fiber filters, they present a serious interference problem when attempting to identify trace inorganic components. To overcome this background problem, samples were collected on cellulose ester fibers, which have a very low background. The results of this analysis, including comparisons of x-ray line intensity, provides an indication of elements present and relative metal concentration.

Sample No.	Line Intensity	Element
NI-47-1	Strong	Pb,Zn
	Medium	Sn,Br
	Weak	K,S,Fe,Cu,Cl,Cd
NI-47-1 (Combusted)	Strong	Zn
	Medium	Sn,K
	Weak	Ca,S,Fe,Cu,Cl,Pb
NI-49-1	Strong	Pb,Zn
	Medium	Sn
	Weak	K,Si,Fe,Cu,Cd,Br

In comparison to the catch on glass fiber filters, there appears to be a lower level of K, Ca, S and probably Cl. Combustion of the cellulose ester filter apparently drives off most of the Pb and Br. The other elements do not exhibit much change in intensity.

(Note: These x-ray fluorescence scans were obtained from 1/4-inch diameter pieces cut from the center and periphery of filter Sample NI-43-1. The two sample pieces yielded identical results, indicating a uniform distribution of elements over the 4-inch diameter filter.)

Finally, to obtain a sense of the amount of organic matter present in the sample, a 1" square sample of filter NI-27-1 was analyzed for total carbon via microchemical determination. A maximum of 3% carbon (both organic and inorganic) was found by this approach--indicating a low level of organic matter.

B. Inorganic Compound Identification

X-ray diffraction (XRD) patterns were obtained from several of the heavily-loaded filters, including NI-27, -32, -35, -38, -42 and -43. The patterns were all quite similar. With the exception of NaCl, which was occasionally present, the patterns, although rich in lines, were not solved with regard to identity of compounds present. To aid in this study, a portion of NI-43-1 was heated to 800°C for 15 minutes after which the sample changed color from the original jet black to a pale straw color. A diffraction scan of the heated sample yielded a few lines which were identified as Zn_2SiO_4. However, because the sample was on a glass fiber filter, it was impossible to determine whether the silicate phase came from a reaction with the glass fiber filter or from silica in the sample. Therefore, for comparison to these studies, a cellulose ester filter (NI-47-1) was analyzed by XRD. This yielded the presence of NaCl and the characteristic, unidentified diffraction pattern observed previously. An ashed sample from this filter exhibited a pale yellow color and provided an x-ray diffraction pattern that was identified as 65% Zn_2SiO_4 - 35% Zn_2TiO_4. The formation of the silicate phase upon heating to 800°C is thus confirmed and apparently was not related to the presence of a glass fiber filter. The presence of medium levels of K and Sn in this ashed sample as determined by XRF (see above) is not accounted for in the diffraction results; it is concluded that there is sufficient silica to form a SiO_2-K_2O-PbO non-crystalline glassy phase.

To help in the identification process, infrared analyses were made for organics on the filter catch and probe washings for several runs: NI-1, 2, 3, 9 and 10. The filter catch was sampled by lightly tapping the filter to dislodge about 1 mg of particulate which was then analyzed using KBr disc techniques. It is recognized that any condensed liquid droplets on the filter would not have been included in the infrared sample by the sampling procedure that was used. The results were consistent for all samples and only gave an indication for the presence of sulfate in all of the probe washings and filters. From these results, it is unlikely that organic material was present in the samples at concentration levels greater than 10-20%.

Incinerator samples 9-1, 9-2, 9-3, 2-1 and 2-2 were examined by TGA and DTA (TGA - thermal gravimetric analysis; DTA - differential thermal analysis) in an effort to provide information about the inorganic material through thermal decomposition or dehydration at specific temperatures. Ideally, one would hope to observe successive weight losses corresponding to loss of water, CO_2, SO_2, etc. The results of the thermal analyses were essentially negative in terms of providing a really useful means for providing quantitative data. In the case of filter sample 2-1, the TGA results showed no weight change (when heated in nitrogen) over the range 50° to 1000°C. The probe and cyclone residue sample (2-2) showed a small weight gain between 300-400°C followed by a gradual weight loss. There was no net weight change after heating up to 1000°C. The same sample was run in air and showed a gradual weight loss from 50-450°C (corresponding to approximately 30% of the sample weight); this loss could not be specifically related to a phase transformation such as dehydration. The DTA analyses on each of the samples showed only minor bumps and wiggles; there was no reproducible endotherms or exotherms that one could interpret in a meaningful manner. Therefore, it was not possible to identify specific compounds in the samples by DTA or TGA.

C. Identification of Organic Material

To better understand the organic character of the particulate, two sets of filter and probe washings were extracted with organic solvents and examined for their organic material content by infrared spectrometric analysis. To do this, the filter samples were extracted sequentially with 20 ml portions of hexane, then chloroform, and finally methanol. Each solvent extract was evaporated to dryness under nitrogen and subjected to IR analysis via the KBr disc technique. (A similar approach was used for the residues from the probe washings but due to smaller sample sizes, the solvent volume used for extraction varied from 2 to 25 ml.) The results are shown in Table E-3. Clearly, only small portions of these samples are organic in nature and soluble in these solvents.

TABLE E-3

Examination of Filter and Probe Washings for Organics

Code	Type	Weight	Hexane	Chloroform	Methanol	Hexane	Chloroform	Methanol	Solvent Extract		Found
NI-5-1	Filter	283	0.6	0.8	88	0.2	0.3	31	Hexane	-	Silicone
									Chloroform	-	Silicone, Hydrocarbon Carbonyl
NI-9-1	Filter	263	0.3	0.4	87	0.1	0.2	33	Methanol	-	Ammonium
NI-5-2	Probe	23	0.2	0.07	1.9	1	0.3	8	Hexane	-	Hydrocarbon
									Chloroform	-	Not Run
NI-9-2	Probe	14	0.1	0.06	2	0.8	0.5	15	Methanol	-	Carbonyl (possibly acetone residue) and Hydroxyl

The filter catch of samples NI-2-1 and NI-9-1 was examined by high resolution mass spectrometry (HRMS) in an effort to gain more insight into the composition of the material collected on the filters. The samples were obtained by tapping the filters to obtain sufficient material (substantially less than 1 mg) for testing. The samples were placed in a small glass capillary and introduced into the direct insertion probe of the mass spectrometer where the temperature of the sample was gradually increased from about 70°C to approximately 250°C. In effect, this procedure causes a fractional distillation of multi-component samples. Spectra are recorded for anything present in the sample which could exhibit a vapor pressure of at least 10^{-7} torr at these temperatures.

For each of the samples, spectra were recorded for a low temperature (80-150°C) and a high temperature (170-250°C) region. The photoplate data were reduced by a computer system, and an elemental composition listing of all the species observed in the spectra was generated. The computer was allowed to search for all combinations of carbon and hydrogen, including up to one nitrogen atom and four oxygen atoms.

Very little material was observed to vaporize from these samples, consistent again with our other analyses. These results indicate that most of the filter catch is inorganic material. The predominant vapor species observed in all four spectra (two samples at two temperatures) were typical hydrocarbons, both aliphatic and aromatic hydrocarbon species being represented. At the higher temperature (170-250°C) $ZnCl_2$ and ZnClBr were observed for Sample 2-1. HBr, apparently due to decomposition of a bromide, was also observed at this temperature. There was an occasional indication of some nitrogenous species in both samples.

In Sample 9-1, an occasional aliphatic nitrogen specie was observed which could be indicative of the presence of some proteinacious-type material on the filter. One of the prominent species in all instances was diethylphthalate. Phthalates as a whole are incidious impurities in most laboratory samples that can generally be attributed to plastic containers, tubing, etc. In this instance, there is some difficulty in ascribing the source of the phthalate since, to the best of our knowledge, the filter paper was always handled so as not to be contaminated from plastic containers and the sample was obtained by direct transfer from the paper onto aluminum foil and into the glass capillary. Our experience leads us to believe that the plasticizer was an impurity; however, the outside chance does exist that it was condensible species actually collected on the filter from the incinerator. There certainly was no shortage of phthalate plasticizers in the plastic materials being burned in the incinerator. Several trace aromatic oxygenated species were also observed in the spectra.

One group of species expected to be present in the particulates, due to their high boiling point, were the polynuclear aromatic hydrocarbons. There was no evidence of these material in any of the samples. The experimental technique employed in these measurements had a detectability for polynuclears in the ppm range. If the PNA's were present in the filter catch, they existed in the ppm concentration range.

D. Development of Approach for Quantitative Analysis Scheme

The results of the preliminary approach to a quantitative analysis scheme are discussed briefly in the following paragraphs.

Several samples were collected at the continuous grate incinerator facility using organic membrane filters (millipore SSWP 04700). Because only 33 mg of particulate was collected on each filter, two were combined and treated as follows: (two blank filters were treated at the same time in an identical manner).

The two filters (NI-54 and NI-56) were combined and leached with 50 ml of hot water for 10 minutes. The leach liquor and subsequent hot water washings were filtered through a dry filter into a 100 ml vol. flask. This filtrate was cooled and diluted to the mark (the solutions were coded FC for sample and FB for blank). The filters were fused in platinum crucibles with 6 g sodium carbonate. Then the fusion was dissolved in water and nitric acid, filtered* and diluted to 100 ml (these solutions were coded FC/F for sample and FB/B for blank).

The two leachate solutions (FB and FC) were analyzed for R_2O_3 sulfate, chloride, acidity and selected cations. The dissolved fusion mix was analyzed for sulfate, R_2O_3, and selected cations (see Table E-4). In addition to this data, a high efficiency glass filter containing catch material (NI-45-1) was analyzed for moisture and ash content of the filter catch. The original sample was very hydroscopic. However, loss at 105°C (moisture) was 2%, and loss after ignition at 800°C was 25% of the drierite dried catch. This represents a residual ash content of 75%. Decomposition of nitrates, halides and others could represent the difference, but the composition of the volatile is unknown. A blank filter showed less than 1% weight loss at 850°C.

E. Conclusion

The filter catch seems to be almost totally mineral type particulate. There does not appear to be much free acid (HCl or H_2SO_4 nor is there much sulfate. R_2O_3 type compounds (Fe, Al, Ti, Zr, Cr, etc.) and silica seem to account for much of the sample. A composite picture of the filter catch based on these preliminary studies is given in Table E-5.

---

*At this point, there was no residue in the blank but the sample contained a trace of reddish brown residue similar to Fe_2O_3.

TABLE E-4

Chemical Analysis of Filter Catch

Nature of Sample		2 blank filters (millipore SSWP04700)	NI-54 NI-56	32.6 mg 32.7 mg
Hot Water Leach	**Units***			
Acidity	meq	<0.05	0.3	
Sulfate	mg	<1	1.3	(0.03 meq)
Chloride	mg	<1	10.6	
R_2O_3		<1	<1	
Cations	mg			
Ca		<0.01	0.2	
Mg		<0.01	0.03	
K		<0.01	20.5	
Na		<0.05	3.0	
Pb		<0.01	0.3	
Zn		<0.01	9.3	
Filter Fusion				
Sulfate	mg	<1	<1	
R_2O_3 (+SiO_2TiO_2)		--	33	
Cations	mg			
Pb		<0.05	1.3	
Zn		<0.05	3.5	

*Units - mg = milligrams; meq = milliequivalents.

TABLE E-5

Composition of Filter Catch

		Glass		Membrane						
	Units*	45	47	54/56	55	57	69A	69D	Blank	Range
Volatile Matter										
Loss @ 105°C	%	3	--	--	7	--	1	1	1	1-7
Loss @ 850°C	%	24	32	--	--	--	--	--	--	24-32
Acidity	meq	--	--	0.3	--	--	0.05	--	<0.1	<.5
Anions	%									
Sulfate		--	--	2	<5	10	17	--	<1	2-17
Chloride		--	--	24	--	26	5	--	1	5-26
Non R_2O_3 Cations	%									
Potassium		--	--	30	3	5	--	--	<1	3-30
Sodium		--	--	4	--	--	--	--	<1	4
Zinc		--	--	19	16	8	--	--	<1	8-19
Lead		--	--	2	--	--	--	--	<1	2
Other (Ca, Mg)		--	--	1	<1	<1	--	--	<1	1
Total		--	--	56	19	13	--	--		13-56
R_2O_3	%	--	--	50	51	60	20	--	<1	20-60
SiO_2 (Acid insol)	%	--	--	--	3	20	4	--	<1	5
Total				65	--	--	44	77	5-10	44-77

*Units - meq = milliequivalents; % = weight percent.

II. IMPINGER RESIDUE

Most of the data reflecting on the composition of the impinger catch is given in Appendix F. However, a few qualitative examinations were conducted early in the program to help guide our quantitative analysis. The results of x-ray fluorescence analyses on the residue from the impinger catch was given in Table E-1. It is clear that this material was quite different in composition from the probe and filter catch. In fact, the high sulfur values, along with the low pH, was an early clue that sulfuric acid may be a predominant specie. Emission spectrographic examination of the impinger residue also showed differences from the probe and filter catch (see Table E-2). For the material collected, aluminum, boron, calcium, chromium, silicon, sodium and zinc seemed to be most prevelant. (This does not include HCl trapped but lost during evaporation step to obtain impinger residue.)

Using infrared techniques, the organic extract from the impinger solutions was identified as containing hydrocarbons, oxidized hydrocarbons, carboxylic acids, ammonium ion and sulfate. (As the infrared spectra was obtained via the KBr disc technique, any free sulfuric acid would be converted to $KHSO_4$ or K_2SO_4.) The relative amounts of organic extractibles from the impinger solutions was extremely small so that it was not deemed necessary to follow-up on these findings and make positive identification of these trace organic components in the impinger catch.

In addition to the above qualitative examination, a number of samples of impinger catch were analyzed quantitatively during the preliminary phases of this program. A composite tabulation of these results is given in Table E-6.

From this data, it was concluded that the impinger catch was probably mineral acid with very little traditional mineral particulate.

TABLE E-6

Analysis of Impinger Solutions

Sample		Hydrogen^{a,b} Ion Conc.	Sulfate			Chloride		Total	R_2O_3^{c}	NH_3^{d}	Total Calcium, Sodium, Potassium	Residual Solids (mg)	
Code	Description	(meq)	ppt'n (mg)	Titration (mg)	(meq)	mg	(meq)	(meq)	(mg)	(mg)	(mg)	Via Drying Over Drierite	After Ignition @ 800°C
NI-13	After evaporation to dryness	--	--	15	0.31	0.9	0.03	--	--	--	0.4	26	--
-13A	After evaporation to dryness	--	--	8.9	0.25	0.5	0.01	--	--	--	0.1	23	--
NI-18^{1}	After evaporation to dryness	--	--	11.6	0.24	0.5	0.01	--	--	--	0.9	20	--
NI-18A	After evaporation to dryness	--	--	16.8	0.35	1.2	0.03	--	--	--	0.2	31	--
NI-6	After concentration to 100ml	5.4	37.8	37.9	0.81	188	5.3	6.1	1.2	--	--	--	--
NI-7	After concentration to 100ml	3.0	26.3	27.6	0.6	101	2.8	3.4	5.6	--	--	--	--
NI-20	After concentration to 100ml	1.7	12.7	21.8	0.27-.45	71	2.0	2.3-2.5	--	--	--	--	--
-20A	After concentration to 100ml	1.5	6.2	16.3	0.1 -0.3	50	1.4	1.5-1.7	--	--	--	--	--
NI-30	After concentration to <10ml	--	--	--	--	--	--	--	--	0.9	--	--	--
NI-34	After concentration to <10ml	--	--	--	--	--	--	--	--	0.5	--	--	--
NI-39	As Received	4.5	--	--	--	--	--	--	--	--	--	--	--
	After concentration to 100ml	4.05	15.0	--	0.32	173	4.9	5.2	3.0	--	--	35	1.3
NI-40	As Received	6.54	--	--	--	--	--	--	--	--	--	--	--
	After concentration to 100ml	6.85	23.3	--	0.48	272	8.0	8.5	3.4	--	--	31	2.4

NOTES

a - By titration with 0.01N NaOH to phenolphthalein end-point.

b - **Meq = milliequivalents.** One meq is the weight in milligrams of the substance (chloride or sulfate) which will react with one mole of hydrogen ion. This is a convenient way to put cations and anions on an equivalent basis.

c - R_2O_3 is an indicator of trivalent and tetravalent cations such as Al^{+++}, Fe^{+++}, Ti^{+++}, etc.

d - NH_3 determined by titration with HCl after distillation from NaOH.

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APPENDIX F

QUANTITATIVE ANALYSIS OF PARTICULATE CATCH

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APPENDIX F

QUANTITATIVE ANALYSIS OF PARTICULATE CATCH

In order to confirm the overall description obtained from the qualitative examination, tests were run with the objective of obtaining quantitative data on the exact composition of the particulate catch.

The basic goal of these quantitative studies was to learn exactly the types and relative amounts of the chemical substances that were being collected in the sampling train. To do this required collecting as large a sample as reasonably possible and then using analytical techniques which permitted a maximum of information with a minimum consumption of the collected sample. Unfortunately, many techniques, especially the so-called wet chemical methods, require a fairly large amount of sample in order to obtain reliable quantitative results. This is especially true when precipitation methods must be used.

In any case, the samples were analyzed using a variety of techniques, recognizing the trade-offs required for obtaining quantitative data on major components at the sacrifice of not being able to analyze for other substances present at lower concentrations.

I. PRELIMINARY STUDY

As a first step in this task, larger-than-normal samples of impinger catch were obtained and analyzed. The impinger catch samples were:

Original Source		Combined
Code	Volume (ml)	Volume (ml)
NI-37-3	930	930
NI-41-3	540	1230
NI-43-3	690	
NI-45-3	500	1175
NI-46-3	675	

These solutions were evaporated in open beakers on a hot plate to slightly under 100 ml and then diluted back to that volume with distilled water. All subsequent analyses were made on aliquots of these solutions. Analyses included: acidity (titration), sulfate (precipitation), R_2O_3 (precipitation), chloride (titration), selected cations (via atomic adsorption spectrometry), ash @ 800°C, and material extractible with ether and chloroform. The results are shown in Table F-1. It is clear from this work that the impinger catch from the continuous grate incinerator was almost totally mineral acid with little else present.

TABLE F-1

Analysis of Impinger Catch from Continuous Grate Incinerators

Component	Units$^{\Delta}$	Sample No. 37-3	Sample No. 41-3/43-3	Sample No. 45-3/36-3
Cations	meq.			
H^+ (acidity)		15.0	12.3	12.0
Other*		<0.1	<0.1	<0.1
Total (max.)		15.1	12.4	12.1
Anions	meq.			
Sulfate		0.9	1.2	1.0
Chloride		14.8	12.9	12.0
Total		15.7	14.1	13.0
Organic Extractible	mg	<2	<2	<2
Ash @ 850°C	mg	<2	<2	<2

*Other cations were present as follows: (milligrams)

	37-3	41-3/43-3	45-3/36-3
Calcium	0.2	0.5	0.2
Magnesium	0.04	0.07	0.03
Potassium	0.1	0.1	0.1
Sodium	0.3	0.4	0.2
Lead	0.06	0.1	0.2
Zinc	0.05	0.05	0.05
Total	0.8	1.2	0.8

Δmeq = milliequivalents; mg - milligrams.

While it is recognized that examination of the effluent from two sources is not in any sense representative of all incinerators, it was felt to be of value to study the emissions from another incinerator. Therefore, several samples of impinger catch were collected via the EPA train procedure at a batch incinerator and quantitatively analyzed. The results are presented in Table F-2. As was found previously, sulfuric and hydrochloric acid were the main components of the impinger catch. A comparison summary of the two incinerators where all of the data has been calculated on the basis of a 1.5 m^3 sample is given in Table F-3. It is clear from this data that the collected "particulate" is similar from both incinerators. The batch unit does have slightly more organic matter and a little less sulfate in the impingers, but mineral acid is the major component being collected by the impingers in both cases.

II. COMPREHENSIVE ANALYSIS OF PARTICULATE CATCH

To help complete our understanding of the composition of the particulate catch, a detailed chemical characterization of four samples of particulate catch from a continuous grate incinerator was carried out. The goal of this part of our program was to obtain a thorough understanding of the composition of the particulate catch collected in each portion of the EPA sampling train.

A. Experimental Procedure

To do this, four samples were collected via the normal EPA sampling procedure, except that:

- The sampling was only continued for 28-44 minutes rather than one hour so that the sample sizes were 35-40 percent of our normal runs;
- Organic membrane filters were substituted for glass filters in two of the runs. This was done to permit a chemical analysis of the filter catch without being faced with a high blank level for the cations and anions of interest. (Note: For details on sampling conditions, see Runs Nos. NI-77 through 80 in Table D-7 of Appendix D.)

The distribution of particulate for the runs with glass filters are not significantly different than those with the membrane filters, but the amount of particulate collected has a wider variation and higher average level than previous runs. The average percentage distribution between probe plus filter versus impingers is consistent with our earlier findings, but the probe plus cyclone collected more of the "traditional" particulate catch (catch in probe, cyclone and filter) in this latest series.

Once collected, the experimental procedures utilized for analyzing these samples were as follows:

TABLE F-2

Analysis of Impinger Catch from Batch Incinerator

Component	Units$^{\Delta}$	Sample Code (BI-)					
		71-3	72-3	73-3	74-3	75-3	76-3
Impinger Catch via EPA Procedure	mg						
Water Soluble		--	--	31	11	16	24
Organo Soluble		--	--	11	9	11	3
Acetone Rinse		--	--	8	6	9	9
Total		--	--	50	26	36	36
SO_2 (via I_2)	mg	--	--	<2	<2	<2	<2
Solids	mg						
@ 105°C		22	30	--	--	--	--
@ 850°C		0.8	2.4	<5	<5	--	--
R_2O_3	mg	--	--	<1	<1	--	--
Anions							
Sulfate	mg	10	13	12	13	--	--
Sulfate	meq	0.2	0.3	0.3	0.3	--	--
Chloride	mg	108	136	127	112	--	--
Chloride	meq	3.1	3.9	3.5	3.2	--	--
Total	meq	3.3	4.2	3.8	3.5	--	--
Acidity	meq	3.5,3.4	4.3,4.0	4.4	3.8	--	--

$^{\Delta}$Units: meq = milliequivalent; mg = milligram.

TABLE F-3

Comparison Summary for Particulate Catch from Two Incinerators

	Average Values* for			
	Continuous Grate		Batch	
	mg	%	mg	%
Results via EPA Procedure:				
Total Weight of Particulate	407	100	305	100
Distribution of Particulate				
Catch Before Filter	77	19	34	11
Filter Catch	272	67	234	76
Combined Total	349	86	268	87
Impinger Catch				
Water Soluble	45	11	21	7
Organic Extract	4	1	8	3
Acetone Rinse	8	2	8	3
Combined Total	57	14	37	13
Weight Per Volume Sampled (mg/m^3)	271		203	
Chemical Analysis of Impinger Catch				
As Received				
Sulfate	19	10	12	8+
Chloride	160	86	121	82
Ash	1+	--	1+	--
Acid (meq)	(5.1)	—	(4.0)	--
Organic (est)	6	3	12	8+
Total (est)	186	--	146	--
After Evaporation to "Dryness" (Drierite)				
Sulfate	19	46	12	32+
Chloride	1	2+	1	2+
Ash	1	2+	1	2+
Organic (est. total)	7	17	12	32+
Water (est)	13	32	11	30
Total (est)	41		37	

*All values converted to basis of 1.5 m^3 sample.

- Acetone Washings of Nozzle and Probe

The samples were transferred to platinum dishes, evaporated to dryness with nitrogen, equilibrated in a drierite desiccator and weighed. They were then dried at 105°C and reweighed. Following this, the sample was extracted three times with 50 ml hot water. The extract was filtered through a 2" millipore membrane filter and combined. The residual solids were collected on the filter and dried. Following this, the extract and solids were treated as shown in Figure F-1.

- Filter Catch

The membrane filters (NI-77 and -79) were dried at 105°C, weighed, extracted three times with hot water, dried at 105°C and then treated as shown in Figure F-1.

The glass filters (NI-78 and-80) were desiccated under drierite, weighed, dried at 105°C and reweighed. These were fused with sodium carbonate and then analyses made for R_2O_3 and sulfate.

- Impinger Catch

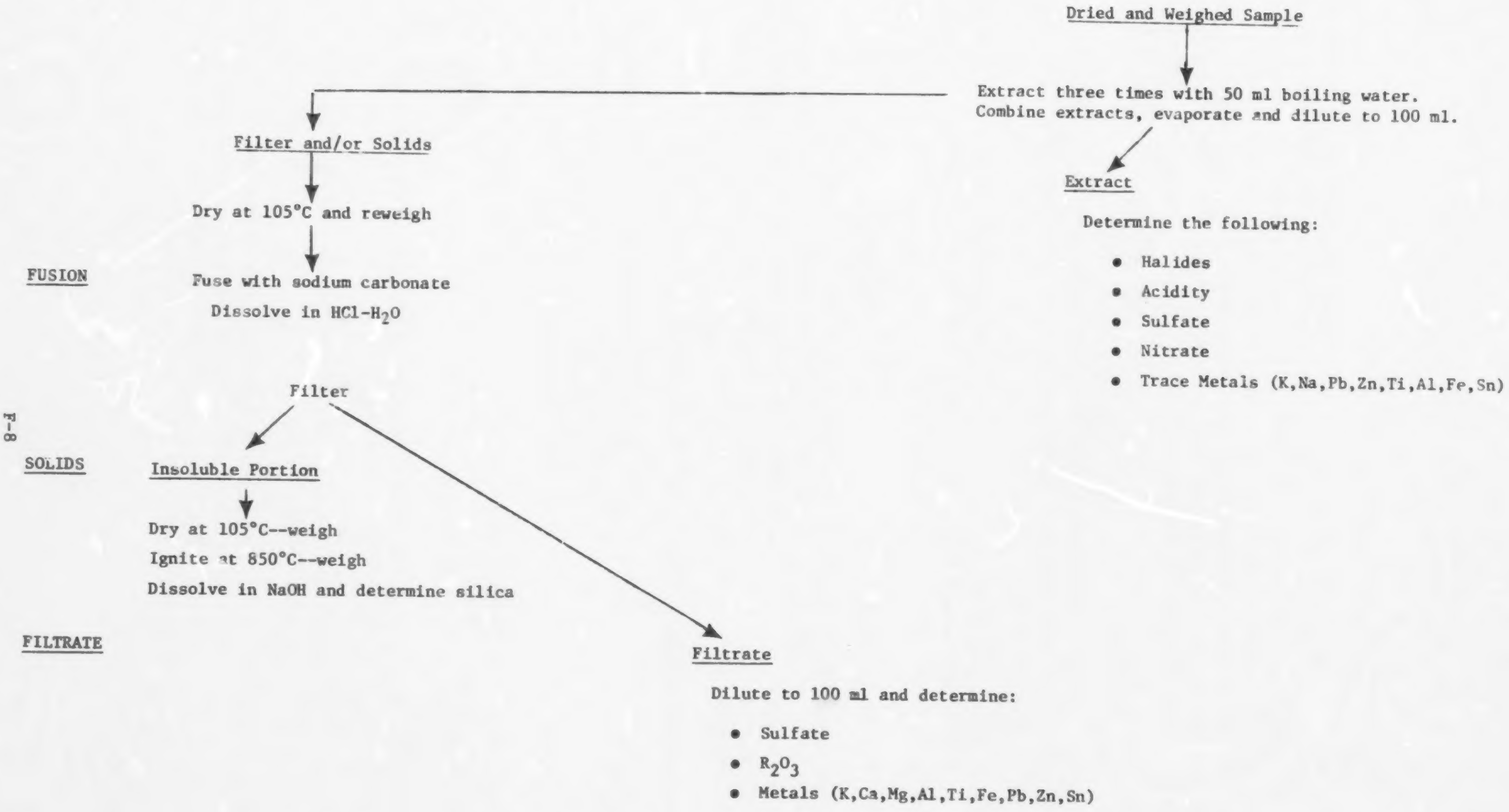
After measuring the volume of each solution, the impinger catch was evaporated, transferred to a 100 ml volumetric flask and diluted to volume with water. These solutions were then analyzed for: acidity, halides, sulfate, nitrate, trace metals (K, Na, Zn, Pb, Ca, Mg, Fe, Sn), organic extractibles, and "dried" solids.

The procedures employed for analyses of these samples were:

Acidity	- Titrate either potentiometrically, or to a phenolphthalein end point, with 0.01 N sodium hydroxide.
Chloride	- Titrate with 0.05 N mercuric nitrate.
Sulfate	- Gravimetrically after precipitation with barium chloride, and in some cases spectrophotometrically via the barium chloranilate procedure.
Nitrate	- Spectrophotometrically using the phenol disulfonic acid (PDS) procedure.
R_2O_3	- Gravimetrically after precipitation with ammonia and ignition to 800°C.
Trace Metals	-Atomic absorption spectrometry using selected source lamps for the elements of interest, including: calcium, magnesium, sodium, potassium, iron, tin, zinc, lead, aluminum and titanium.

FIGURE F-1

Analysis of Solid Catch


Dried and Weighed Sample
Extract three times with 50 ml boiling water.
Combine extracts, evaporate and dilute to 100 ml.
Extract
Determine the following:
• Halides
• Acidity
• Sulfate
• Nitrate
• Trace Metals (K,Na,Pb,Zn,Ti,Al,Fe,Sn)
Filter and/or Solids
Dry at 105°C and reweigh
FUSION
Fuse with sodium carbonate
Dissolve in HCl-H2O
Filter
SOLIDS
Insoluble Portion
Dry at 105°C--weigh
Ignite at 850°C--weigh
Dissolve in NaOH and determine silica
FILTRATE
Filtrate
Dilute to 100 ml and determine:
• Sulfate
• R2O3
• Metals (K,Ca,Mg,Al,Ti,Fe,Pb,Zn,Sn)

B. Results and Discussion

1. Catch in Probe and Cyclone

With these samples, we attempted to obtain as comprehensive an analysis as possible so that a proper material balance on the composition of the catch could be derived. Unfortunately, the small size of the sample as well as its chemical complexity made this a difficult goal and one that was not completely attained. However, in spite of these limitations, it was possible to derive a good picture of the nature of the probe catches (see Tables F-4 through F-6). Some observations on this data for the probe catch are:

- As evidenced by an examination of Table F-5, the overall ratio of the components of the probe catch did not vary appreciably between runs even though there was variation between solubles and insolubles. The major cation constituents (>10%) were calcium, zinc, potassium, sodium, and aluminum.

- Distribution of the measured constituents is also quite consistent (Table F-6). Cations make up about 50% by weight of the total probe catch. The quantity of anions determined is low in NI-78-2 and possibly 79-2 and 80-2. Some of the cations may have been present as oxides--an anion which was not determined via analysis.

- Even though hot water solubles varied appreciable (24-60%), their composition did not seem to change except that total measured anions were lower with lower percentage of solubles. This could be related to presence of ignited oxides--which are insoluble and have oxygen as the anion.

2. Filter Catch

A similar effort to that for the material caught in the probe and cyclone was devoted to the filter catch. The results of our analyses on the filter catch are given in Tables F-7 through F-9. Because the glass filters were known to contain impurities, complete data was obtained only on NI-77-1 and NI-79-1 where membrane filters had been employed. As shown in Table F-7, the materials balance for NI-77-1 is poor (almost twice by combining the analyses for individual components as actually collected). Possibly because of this, the agreement between the two runs, NI-77 and NI-79, is not overly good. Thus, in Table F-8, which gives the distribution of the filter catch between analysis categories, there is poor agreement. However, Table F-9, which shows the relative levels of the individual cation components, indicates reasonable consistency except for lead, potassium and sodium.

TABLE F-4

Analysis of Probe Plus Cyclone Catch

Code (NI-)	Unit$^{\Delta}$	Analysis Results*				
		77-2	78-2	79-2	80-2	Blank
Weight of Catch						
Dried over Drierite	mg	32	82	107	52	---
Dried @ 105°C	mg	30	80	105	50	---
Hot Water Solubles						
Weight	mg	18	19	47	19	1
Percent of Catch	%	60	24	45	38	---
Free Acidity	meq	<0.1	<0.1	<0.1	<0.1	<0.1
Cations	mg					
Zinc		1.5	1.7	1.7	2.3	<0.05
Lead		<0.05	<0.05	<0.06	<0.06	<0.05
Tin		<0.5	<0.5	<0.5	<0.5	<0.5
Iron		<0.1	<0.1	<0.1	<0.1	<0.1
Potassium		1.0	1.8	3.0	2.8	<0.02
Sodium		0.9	1.5	2.5	2.1	<0.05
Titanium		<0.05	<0.05	<0.05	<0.05	<0.05
Aluminum		<0.05	<0.05	<0.05	<0.05	<0.05
Total Cations		3.4	5	7.2	7.3	1
Anions	mg					
Chloride		4	5	12	7	1
Sulfate		5	5	5	5	1
Nitrate		<1	<1	<1	<1	<1
Total Anions		9	10	17	12	<1
Total Measured Solubles	mg	12	15	24	19	1
Ratio of Components Determined by Measurement of amount Extracted		0.7	0.7	0.5	1	---

TABLE F-4 (Continued)

	Unit	Analysis Results[*]				
		77-2	78-2	79-2	80-2	Blank
Hot Water Insolubles						
Weight (by difference)	mg	12	61	58	31	---
Acid Insolubles After Fusion	mg	2	7	14	3	---
Cations	mg					
Calcium		0.6	3.2	6.9	4.4	0.1
Magnesium		0.09	0.9	1.4	0.5	0.05
Zinc		0.09	1.3	1.8	0.7	0.2
Lead		0.2	0.8	1.7	1.2	0.3
Tin		<0.5	<0.5	<0.5	<0.5	<0.5
Iron		0.6	1.4	1.6	0.6	0.05
Potassium		0.2	1.1	0.9	0.5	0.1
Titanium		0.4	1.8	1.2	0.7	0.05
Aluminum		0.9	5.0	4.2	1.9	0.1
Total Cations		3.1	15.5	19.7	10.5	---
R_2O_3	mg	16	40	31	18	4
Anions	mg					
Sulfate		0-8	3-6	3-13	1-8	0-17
Silicate		<0.5	5	10	<0.5	0.9
Total Soluble and Insoluble	mg					
Hot Water Solubles						
Cations by AA		3.4	5	7.2	7.3	
Anions		9	10	17	12	
Insolubles						
Fusion Insolubles		2	7	14	3	
Cations by AA		3.1	15.5	19.7	10.5	
Anions		6	9	20	5	
R_2O_3 Cations[+]		8	20	16	9	
Combined Total		32	66	94	47	
Percentage Recovered[++]		100	80	87	91	

[*] All values have been corrected for measured blank levels where possible

[Δ] Units are: mg = milligram; meq = milliequivalents; % = weight percent.

[+] In calculating, assume 50% of R_2O_3 is cations by weight.

[++] Combined total divided by weight of catch.

TABLE F-5

Relative Levels of Individual Components of Probe and Cyclone Catch

Element	Amount in Sample mg (%)*								Average Composition	
	77-2		78-2		79-2		80-2		mg	%
Cations										
Calcium	0.6	(9)	3.2	(16)	6.9	(26)	4.4	(25)	15.1	21
Magnesium	0.09	(1)	0.9	(4)	1.4	(5)	0.5	(3)	2.9	4
Zinc	1.6	(25)	3.0	(15)	3.5	(13)	3.0	(17)	11.1	15
Lead	0.2	(3)	0.8	(4)	1.7	(6)	1.3	(7)	4.0	5
Tin	<0.5		<0.5		<0.5		<0.5		0.5	1
Iron	0.6	(9)	1.4	(7)	1.6	(6)	0.6	(3)	4.2	6
Potassium	1.2	(18)	3.9	(14)	3.9	(14)	3.3	(19)	12.3	17
Sodium	0.9	(14)	1.5	(7)	2.5	(9)	2.1	(12)	7.0	10
Titanium	0.4	(6)	1.8	(9)	1.2	(4)	0.7	(4)	3.9	5
Aluminum	0.9	(14)	5.0	(24)	4.2	(16)	1.9	(11)	12.0	17
Total	6.5	(100)	21.5	(100)	26.9	(100)	17.8	(100)	72.7	

* Listed numbers are milligrams found. Values in parenthesis are relative percent of element to total cation levels in the probe catch.

TABLE F-6

Distribution Within Probe/Cyclone Catch

Component	Amount in Sample mg (%)*							
	77-2		78-2		79-2		80-2	
Total Collected Catch	30	(100)	80	(100)	105	(100)	50	(100)
Hot Water Solubles	18	(60)	19	(24)	47	(45)	19	(38)
Cations								
Determined by AAS$^{\Delta}$	6.5	(22)	20.5	(26)	27	(26)	18	(36)
Calculated from $R_2O_3$$^{+}$	8	(26)	20	(25)	16	(15)	9	(18)
Total	14.5	(48)	40.5	(51)	43	(41)	27	(54)
Anions								
Sulfate	11	(37)	9	(11)	15	(14)	10	(20)
Chloride	4	(13)	5	(6)	12	(11)	7	(14)
Total (incl. silicate)	5	(50)	19	(24)	37	(35)	17	(34)
Acid Insolubles	2	(7)	7	(9)	14	(13)	3	(6)
Total by Analysis (cations, anions, acid insolubles)	31.5	(105)	66.5	(83)	94	(90)	47	(94)

* Values in parenthesis are relative percent to total probe catch.

Δ Atomic absorption spectrometry.

+ R_2O_3 represents cations precipitated with ammonia. For purposes of this table, 50% of measured R_2O_3 was assumed to be due to cations.

TABLE F-7

Analysis of Filter Catch

Code (NI-)	Unit[*]	Results Found				
		77-1	78-1	79-1	80-1	Blank
Filter Type		Membrane	Glass	Membrane	Glass	---
Weight of Catch	mg					
Dried over Drierite		50	153	124	108	---
Dried at 105°C		41	---	110	---	---
Hot Water Solubles						
Weight (by difference)	mg	33	---	78	---	10
Percent		80	---	71	---	---
Free Acidity	meq	0.2	---	0.4	---	0.1
Cations via AAS	mg					
Calcium		---		---		---
Magnesium		---		---		---
Zinc		6.6		6.6		<0.05
Lead		0.2		0.4		<0.05
Tin		< 0.5		<0.5		<0.5
Iron		< 0.01		0.01		<0.01
Potassium		12		3.7		<0.05
Sodium		3.5		7.3		<0.1
Titanium		<0.05		<0.05		<0.05
Aluminum		<0.05		0.3		<0.05
Total		22.3		18.3		
Anions	mg					
Chloride		14		31		<1
Sulfate		13		11		17
Nitrate		<1		<1		<1
Total		27		42		19
Total Solubles[Δ]						
Measured	mg	49		60		---
Ratio Measured to Extracted		1.5		0.75		---

TABLE F-7 (Continued)

		Results Found				
	Unit*	77-1	78-1	79-1	80-1	Blank
Hot Water Insolubles						
Weight	mg	10		32		---
Acid Insolubles After Fusion	mg	1		2		---
Cations	mg					
Calcium		0.05		0.2		0.2
Magnesium		0.05		0.06		0.05
Zinc		0.5		0.8		0.05
Lead		1.4		5.9		0.2
Tin		0.5		0.5		0.5
Iron		0.05		0.5		0.2
Potassium		0.3		0.2		0.2
Titanium		0.1		0.4		0.05
Aluminum		0.2		0.8		0.1
Total		2.5		8.8		---
Anions	mg					
Sulfate		1-5		4-10		
Silicate		0.1		1		0.5
R_2O_3[a]	mg	22		13		5
Total Insolubles[x]	mg		75		95	
Combined Total						
Hot Water Insolubles	mg					
Cations by AAS		22		18		
Anions		27		42		
Insolubles						
Fusion Insolubles		1		2		
Cations by AA		3		9		
Anions		10		11		
R_2O_3		22		13		
Total Found		75		95		
Recovered	%	180		86		

*Units are: mg - milligrams; meq = milliequivalents.
[Δ]Total solubles = total cations plus total anions.
[+]Ratio = Total solubles divided by weight (by difference of hot water solubles).
[x]Total insolubles = fusion insoluvles + cations + anions + R_2O_3.
[a]Assume 0% by weight of R_2O_3 is cation.

TABLE F-8

Distribution Within Filter Catch

Component	Amount in Sample - mg (%)*			
	77-2	78-2	79-2	80-2
Total Collected Catch	41 (100)	135 (100)	110 (100)	98 (100)
Hot Water Solubles	33 (80)	-	78 (71)	-
Cations				
Determined by AAS	24.8 (61)	-	27.1 (25)	-
Calculated from R_2O_3	16 (27)	-	10 (6)	-
Total	41 (88)	-	37 (31)	-
Anions				
Sulfate	16 (39)	25 (19)	18 (16)	9 (11)
Chloride	14 (34)	-	31 (28)	-
Total (including Silicate)	30 (73)	-	50 (45)	-
Acid Insolubles	1 (2)	-	2 (2)	-
Total by Analysis (Cations, Anions, acid Insol.)	72 (175)	-	89 (81)	-

* Values in parentheses are relative percent of total filter catch.

TABLE F-9

Relative Levels of Individual Components of Filter Catch

	Amount in Sample - mg (%)		
Element	**77-2**	**79-2**	**Average**
Calcium	<.05	0.2 (<1)	(<1)
Magnesium	<.05	0.06 (<1)	(<1)
Zinc	7.1 (29)	7.4 (27)	(28)
Lead	1.6 (6)	6.3 (28)	(15)
Tin	0.5 (<1)	0.5 (<1)	(<1)
Iron	0.5 (<1)	0.5 (2)	(1)
Potassium	12.3 (50)	3.9 (14)	(32)
Sodium	3.5 (14)	7.3 (27)	(20)
Titanium	0.1 (<1)	0.4 (1)	(1)
Aluminum	0.2 (<1)	1.1 (4)	(2)
Total (mg)	24.8 (100)	27.1 (100)	

*Values in parentheses are relative percent of element to total cation levels in the filter catch.

3. Comparison of Probe/Cyclone and Filter Catches

In order to obtain an indication as to whether the composition of the filter catch was different than that found in the probe and cyclone, the averages for each set of data were compared (see Table F-10). In looking at this table, it must be remembered that the averages represent a wide range between the individual results. This may represent a special problem for the filter values because the values for NI-77-1 add up to 175% of the original sample. However, in spite of these reservations, it is constructive to compare the available data.

- Each is primarily inorganic mineral type particulate;
- There is little free acid measured in either sample. Thus, if collected by the solids, the acid reacts to form a more neutral species;
- Sulfate levels seem consistent;
- Chloride is much higher in the filter catch. Although the difference may be due to a lower temperature on the filter, it also may be an artifact because of the use of a solvent evaporation step for preparing the probe catch for analysis. Hydrochloric acid could be distilled out of the sample more easily at that point than during drying of an essentially "dry" filter at 105°C.
- There are more acid insolubles (after sample dissolution) in the probe catch than in the filter catch. Very little silicate was found in the filter catch whereas in two cases (NI-78 and NI-79) some silicate was found in the probe catch. This could explain the difference in the acid insolubles. (Silicate acid should be insoluble and reported as acid insolubles. However, sometimes it remains solubilized and this is the reason it was determined in the filtrate. When silica was found in the filtrate, it almost certainly had to be a major portion of the value reported as acid insolubles reported in Table F-6. However, this potential error does not change our conclusions in any way.
- The relative proportions of individual cations to the total determined by atomic absorption spectrometry shows differences (Table F-11). In particular, a high proportion of calcium and magnesium is in the probe/cyclone catch. (Unfortunately, these elements were not determined in the water soluble portion in either case so that these results may be distorted. However, until further work is done, this possible difference has been noted.) Also, there seems to be more zinc, lead, potassium and sodium on the filter and more aluminum in the probe/cyclone.

TABLE F-10

Comparison of Filter Catch and Probe/Cyclone Catch*

Component	Results (Weight Percent of Total Catch)			
	Probe/Cyclone		Filter	
	Range	Average	Range	Average
Hot Water Solubles	24-60	42	71-80	75
Cations				
Determined by AAS	22-36	28	25-61	44
Calculated from R_2O_3	15-26	21	6-27	17
Total Cations	49		61	
Anions				
Sulfate	11-37	20	11-39	21
Chloride	6-13	11	28-34	31
Total Anions	31		52	
Acid Insolubles	6-13	9	2	2
Total by Analysis	89		115	

*Range and Averages for all runs.

TABLE F-11

Proportion of Individual Cations in Filter and Probe/Cyclone Catches

Element	Results (Percent of Total Cations Measured by AAS)			
	Probe/Cyclone		Filter	
	Range	Average	Range	Average
Calcium	9-26	19	1	1
Magnesium	1-5	3	1	1
Zinc	13-25	18	27-29	28
Lead	3-7	5	5-23	15
Tin	<1	<1	<1	<1
Iron	3-9	6	<1-2	1
Potassium	14-19	16	14-50	32
Sodium	7-14	11	14-27	20
Titanium	4-9	6	<1-1	1
Aluminum	11-24	16	<1-4	2

- A presentation of the distribution of sulfate and chloride between the various parts of the sampling train is given in Table F-12. As can be seen from this data, the sulfate was fairly evenly distributed between the probe/cyclone, filter, and impinger. The total amounts of sulfate collected ranged between 92-155 mg which based on a 1.5 m^3 sample represents 15-25 ppm of sulfur oxides.

- Chloride, on the other hand, was found predominantly in the impingers with half as much on the filter and only a small amount in the probe/cyclone. This may be directly related to the temperature and amount of water available for trapping--i.e., since the probe is hottest, there is less "available water." Also, sulfur trioxide will probably displace any HCl trapped on the filter.

4. Impinger Catch

The results of the detailed chemical analysis of the impinger catch is given in Table F-13. As had been demonstrated in the preliminary quantitative work, the impinger catch was primarily mineral acid (sulfuric acid and hydrochloric acid) with practically no mineral particulate. Thus, the amount (milliequivalents) of sulfate and chloride matches almost exactly the total acidity. Even though a small quantity of sodium, potassium and iron were found, mineral type particulate represented a negligible amount compared to the total catch. Because of the extreme difficulty of characterizing trace quantities of non-extractable organics, the exact nature of the organics in this faction was not determined and thus is unknown. (Typical organics which might have been present include low molecular weight acids, alcohols, ethers, esters, aldehydes, and ketones.)

III. GENERAL COMMENT

By means of this very detailed quantitative analytical program, we were able to generate a good understanding of the composition of the particulate catch. However, the material balance aspects of the results, especially in the case of the filter catch (Table F-7), are not as good as would be desired. Whether this was due to the variation in sample homogeniety, impression of the analytical methods, or presence of unidentified components is not known. It is likely that operating with such small samples the analytical error was sufficiently large to explain the observed differences.

In summary, we concluded that the probe/cyclone catch and filter catch were similar in composition and predominantly inorganic materials. Although each had similar compositions, variations were noted between the probe/cyclone and filter in relative concentrations of some cations as well as sulfate and chloride. The significance of these differences to the use of this sampling train are unknown, but presumed to be small. As noted earlier, the impinger catch is primarily mineral acid, and thus should not contribute to a traditional measure by weight of particulate catch.

TABLE F-12

Distribution of Chloride and Sulfate in Sampling Train

Sample (NI-)	Distribution of Sulfate (%)			Distribution of Chloride (%)		
	Probe/Cyclone	Filter	Impinger	Probe/Cyclone	Filter	Impinger
77	28	40	32	9	32	59
78	16	42	42	--	--	--
79	28	34	38	11	29	60
80	28	26	46	--	--	--
Average	25	35	45	10	30	60

TABLE F-13

Analysis of Impinger Catch

		Results for Sample				
General Source (NI-)	**Unit$^{\Delta}$**	**77-3**	**78-3**	**79-3**	**80-3**	**Blank**
Volume of Gas Sampled	m^3	0.57	0.59	0.53	0.59	---
Volume of Water in Impingers	ml	335	330	345	325	350
Results via EPA Procedure	mg					
Water Solubles		16	---	24	17	---
Organic Extractibles		2	---	2	2	---
Total Impinger Catch						
As received		16	---	24	17	---
on 1 m^3 basis		28	---	45	29	---
Chemical Analysis^{+}						
Acidity	meq	0.9	3.7	2.0	2.5	0.1
Cations	mg					
Calcium		0.05	0.05	0.05	0.05	0.05
Magnesium		0.05	0.05	0.05	0.05	0.05
Zinc		0.05	0.05	0.05	0.05	0.05
Lead		0.05	0.05	0.05	0.05	0.05
Tin		1	1	1	1	1
Iron		0.05	0.05	0.02	0.02	0.01
Potassium		0.03	0.1	0.08	0.04	0.02
Sodium		0.07	0.6	3.4	0.3	0.02
Total Cations		0.2	0.8	3.4	0.4	0.2
Anions	mg					
Sulfate		13	25	20	16	2
Chloride		26	122	64	83	1
Nitrate		0.5	0.7	1.3	0.9	0.1
Total Anions		39	148	85	100	
Materials Balance	meq					
Positive Ions						
Cations		0.1	0.1	0.1	0.1	0.1
Acidity		0.9	3.7	2.0	2.5	0.1
Total		0.9	3.7	2.1	2.5	0.1
Negative Ions						
Sulfate		0.1	0.3	0.2	0.2	0.1
Chloride		0.7	3.4	1.8	2.3	0.1
Nitrate		0.1	0.1	0.1	0.1	0.1
Total		0.8	3.7	2.0	2.5	0.1

+On sample as received and before evaporation to dryness.

Δm^3 = gas sample in cubic meters; mg = weight in milligrams; meq = quantity of component in milliequivalents.

APPENDIX G

HIGH-EFFICIENCY GLASS FIBER FILTER PERFORMANCE CHARACTERISTICS

I. INTRODUCTION

High-efficiency glass fiber filters are commonly used to collect particulates from both ambient air and stack gases. The filter material was developed for the Atomic Energy Commission(1,2) for ventilation applications. It is a felt-like material composed of a combination of glass fibers in mixed sizes (about 0.5 to 3μm).

There are specifications for this filter for processing use (MIL-F-51079A) but not sampling applications. At the present time, two binderless filters (MSA 1106BH and Gelman Type A) have been found the most acceptable for atmospheric sampling and analysis(3,4), and are specified for use in the EPA particulate stack sampling train.

Because significant fractions of particulates collected in the EPA sampling train have been found in the impingers downstream of the filter, the efficiency of the filter has been questioned as follows:

- Is the filter efficiency adequate for aerosol particles smaller than 0.3μm?
- Is the filter efficiency for solid aerosol particles of various densities as good as the tested efficiency for liquid DOP aerosol?
- What are the effects of high temperature on filter performance?
- Do electrostatic charges on the particles and/or filter reduce filter efficiency?

We have evaluated the capability of the filter by a review of previous studies and by experimental incinerator sampling.

Several of the more important properties of filters are described below:

- Efficiency is a measure of the ability of a filter to remove particles from an air stream. Initial efficiencies of new filters are most commonly quoted, but efficiency as a function of filter loading is equally important. Performance is frequently expressed in terms of penetration, which is a measure of the ability of particles to pass through a filter. Percent efficiency equals 100% minus percent penetration.

- Flow resistance is measured by the static pressure drop across a filter at a given flow rate.

- Particle collection capacity or filter loading is the amount of particulate that a filter can hold before flow resistance or penetration become excessive.

The filtration performance of these filters depends on filter composition, particle size, particle loading, and many other factors. However, the following supplier's data on MSA 1106BH with 0.3μm diameter dioctyl phthalate (DOP) liquid aerosol is typical:

Velocity (ft/min)	Initial Efficiency (%)	Flow Resistance (in. H_2O)
10	99.995	1.48 to 1.58
28	99.98	3.94 to 4.33

Linear filtration velocities in the EPA sampling train at 1 CFM are approximately as follows:

Filter Diameter (in.)	Velocity (ft/min)
2-1/4	36
3	24
4	12

II. EFFECT OF VELOCITY AND PARTICLE SIZE ON FILTRATION PERFORMANCE

Figure G-1 shows that flow resistance increases linearly with velocity. Figure G-1 also shows that efficiency decreases with velocity up to about 50 ft/min and then increases. The minimum efficiency point results from the combined effects of particle diffusion and impaction, and varies with filter construction (usually between 30 to 70 ft/min).

The efficiency on particles other than 0.3μm has been the subject of much misunderstanding and controversy. It is commonly thought that the filter collects particles only down to 0.3μm diameter. This misunderstanding results from the common practice of stating 0.3μm DOP efficiences without interpretation. The DOP test was designed during World War II to test high-efficiency gas mask filters against what was thought at that time to be the most penetrating particle size (0.3μm). The most penetrating particle size of these filters is now believed to be between 0.1 and 0.3μm diameter; the peak penetration is about 2 to 3 times the DOP penetration.(5,6,7,17) Particles smaller and larger than the most penetrating are collected with greater efficiency, largely by diffusion and impaction, respectively.

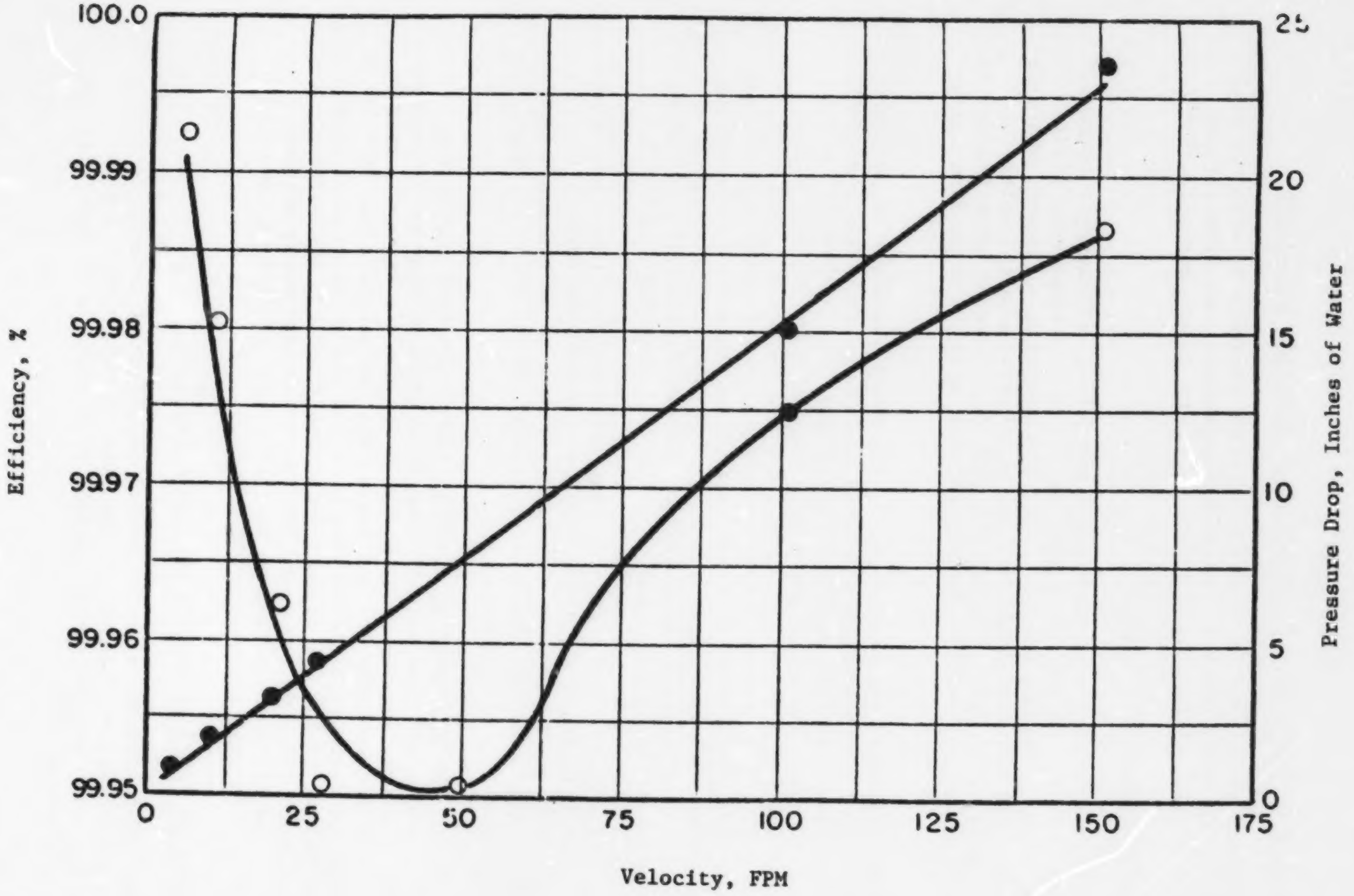


FIGURE G-1

Efficiency of Absolute Filter Vs. Flow Rate
(0.3-Micron Dioctyl Phthalate Aerosol)

● Pressure Drop
○ Efficiency

Source: Reference 11.

III. EFFECT OF SOLID VS. LIQUID AEROSOLS ON FILTER EFFICIENCY

The efficiency of filters for solid vs. liquid aerosols is also not well understood. However, there is reasonable agreement that HEPA filters have equal initial efficiency for both solid and liquid aerosols.(8-10)

IV. FILTER LEAKAGE EXPERIMENTS

As the filter becomes loaded with solid particles, efficiency increases, whereas the reverse is true of liquid particles. Loading with liquid particles is not a common problem with stack sampling. However, where it does occur, HEPA filters should be limited to particulate loadings of about 20 mg/sq cm of surface area.(11) The use of two or more filters in series will increase loading capacity but will also increase flow resistance.

In an effort to learn whether the high-efficiency glass filter is prone to leakage and thus creates an artificially high catch in the impingers, the EPA sampling train was modified by incorporating a glass "T" after the filter holder. The stack gas sample was split by the "T" with one side of the "T" passing in a normal fashion to the EPA impingers while the gas stream from the other side was passed through an auxiliary filter and then to a set of EPA-type impingers. This modified sampling system was then used for direct sampling of incinerator stack gases using MSA 1106BH filters in each side of the train. The data for this work are shown in Table G-1. Based on the fact that the amount of particulate collected on the auxiliary filter was a small percentage of the total collected by the train, it has been concluded that the primary filter is not allowing a significant (>3%) amount of filterable particulate to reach the impingers. Therefore, a back-up filter would have little or no effect on the quantity or quality of the material caught in the impingers.

Efforts to run the EPA sampling train in such a way that the filter became overloaded and thus was more susceptible to leakage were unsuccessful. This was true for two reasons; one being the difficulty in operating the train successfully for 5-6 hours, and the second being that we were unable to reach liquid overloading of the filter by organic tars and oils because of the low organic emissions from this incinerator. The experiments did show, however, that no breakthrough was obtained even after the filter collected up to four times the "normal" amount of particulate. (Normal represents 200-300 mg.)

V. EFFECT OF PARTICLE DENSITY ON FILTER EFFICIENCY

The effect of increased particle density on filter efficiency is to increase efficiency at high velocities, due to impaction. Reduced efficiencies with heavier particles have been measured at low velocities, but not understood.(15)

TABLE G-1

Distribution of Particulate from Filter Leakage Experiments

Run No.*	Dry Gas Volume (meter^3)	Particulate Catch (mg)			Impinger Catch (mg) Collected After		Material on Back-Up Filter as a Percent of	
		Probe and Cyclone	On Filter		Primary Filter	Primary & Back-Up Filter	Probe/Cyclone/ Filter Catch	Impinger Catc
			Primary	Back-up				
NI-11 Primary	1.65	129	785	4	49	52	0.3	8
-11 Auxiliary	2.78			2				
NI-12 Primary	1.49	154	563	15	28	80	2	20-50
-12 Auxiliary	2.64							
NI-13 Primary	0.91	100	246	4	32	33	1.2	12
-13 Auxiliary	0.86							

---

*All runs 60 minutes, sample initially goes through primary filter, then is split so that part goes directly to a set of impingers while other part (aux.) goes through a second filter and then impingers.

VI. EFFECT OF ELEVATED TEMPERATURE ON FILTER PERFORMANCE

This subject is discussed by Dyment(13) as follows:

"At elevated temperature, gas viscosity will increase and therefore increased pressure drops will be obtained for the laminar flow conditions which prevail in high-efficiency paper media under normal ambient conditions.

The effect of temperature on fiber filtration mechanisms has been summarized by Thring and Strauss(14) in terms of inertial, interception and diffusional collection. Because of the way in which the three mechanisms vary with conditions (i.e., fiber and particle sizes, fluid velocity) a general rule cannot be formulated for the effects of temperature on filtration performance. When the predominant mechanism is known, however, the effects can be predicted qualitatively. Inertia and interception efficiency are reduced by increased temperature. For the larger particles for which inertial impaction is more important, changes in particle/fiber adhesion at high temperature may exaggerate or modify this effect. The diffusion mechanism is of increasing importance as particle size diminishes below one micron. For diffusion the effect of temperature rise is to increase the fiber collection efficiency particularly for submicron particles."

Dyment also reported the results of some glass fiber filter tests with sodium chloride aerosol at temperatures up to 500°C. He found that glass paper shrinks at these temperatures so he preheated the samples to avoid cracking failure. His data, while extremely limited, suggest that increasing temperatures to 400°C slightly decreased filter efficiency. His conclusions were as follows:

"In practice the effect of temperature and pressure on filtration mechanism and performance has not been found a determining factor in the application of high-efficiency filters. The main problems are the physical and chemical effects of a high-temperature environment on the materials of construction of the filter, which are manifested by reduced mechanical strength and resilience or loss of adhesion, leading to mechanical leakage and loss in efficiency."

More recent high-temperature filter efficiency tests were reported by First.(15) Heat-shrunk quartz fiber filters were tested at temperatures up to 950°F with sodium chloride aerosols of $0.14\mu m$ mass median diameter at velocities of 15 to 30 cm/sec. No effect of temperature on efficiency was found.

VII. ELECTROSTATIC EFFECTS ON FILTER EFFICIENCY

The effects of electrostatic charges on filtration efficiency are poorly understood. The most commonly reported effects are relatively small increases in efficiency when the particles are charged, and greater increases when the filter is charged.(16,17)

The high-efficiency glass fiber filter is reported to collect at least 99% of charged particles of all sizes in the atmosphere(18,19). Adverse electrostatic effects on filter efficiency may be possible, but appear unlikely.

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APPENDIX H

CHARACTERIZATION OF PARTICULATES DIRECTLY ON THE FILTER

Several sampling runs were conducted for very short times (5 seconds to 5 minutes) to obtain very lightly-loaded filters suitable for optical examination. (Samples were from Runs No. NI-17A, NI-48, and NI-60. Details of sampling conditions are given in Appendix D.) In this way, it was hoped to obtain a typical particle size distribution and further more, through x-ray analysis of isolated particles, to determine systematic variations in particle chemistry as a function of size. For these studies, three filter media were employed, including glass fiber, organic membrane, and silver membrane. Scanning electron micrographs of clean filters of each type are shown in Figure H-1.

Characterization methods included optical examination, scanning electron microscopy (SEM) and non-dispersive x-ray analysis of individual particles in the SEM. In general, the particles were too small to obtain good confirmation by optical microscopy. The excessive surface roughness of the filters combined with the very limited depth of field of the optical microscope made it very difficult to "focus-in" on particles, and accurate descriptions of size and morphology were precluded, even for the organic membrane filters which could be made transparent by a suitable immersion oil and examined in transmission. Therefore, all examinations were conducted with the SEM.

Because of its high electrical conductivity, the silver membrane filter is very stable under electron bombardment in the SEM. The organic membrane and glass fiber filters must be vapor-coated with carbon to avoid building up of space charges and loss of image resolution. A non-dispersive x-ray analyzer attachment to the SEM permits elemental analysis of individual particles and is invaluable for characterizing particle chemistry.

Several typical examples of filter catch particulate are presented in Figures H-2 through H-6. Figure H-2, the glass fiber filter is seen to trap large particles at the surface, whereas smaller particles became embedded. Highly morphological particles are shown in Figure H-3. The qualitative chemical analysis of one of these particles, as determined by non-dispersive x-ray analysis, indicated a chemistry consistent with a mixed potassium calcium sulfate.

In comparison, the collected particle exhibited in Figure H-4 exhibits a morphology very similar to that of the particles shown in Figure H-3. However, the chemistry is quite different, with enrichment in Cl, Al, Si and Zn content and less Ca and S. These examples point out the difficulty in identifying compounds by the methods. Individual particles can have quite different chemistries dependant upon their combustion history. Also, the x-ray intensity of any given element is influenced by the other elements present (matrix absorption and emission effects) and also by the size and geometry of the particle being analyzed. Thus, results are qualitative in nature, and the usefulness of the method depends upon the objective of the analysis.

Other typical collected particles are shown in Figures H-5 and H-6. The spherical glassy slag particle contains many smaller particles on the surface which have a somewhat different chemistry. The fly ash particle has an elemental chemistry very similar to what is observed in gross chemical analysis of filter catches by x-ray fluorescence or emission spectrographic analysis.

Examination of several dozen particles has indicated a similar chemistry for sizes within the range of 2 to 5 μ, with Si, Al, S and Cl being the major species. Based upon this rather limited examination of filter catch samples, we conclude that it is feasible to conduct particle size distribution measurements and corresponding qualitative chemical analysis on all particles down to approximately 1 μm.

Organic Membrane (Millipore Cellulose Ester)

Silver Membrane (Selas Flotronics)

Glass Fiber (MSA)

20µm

FIGURE H-1 Scanning Electron Micrographs of Clean Filter Media

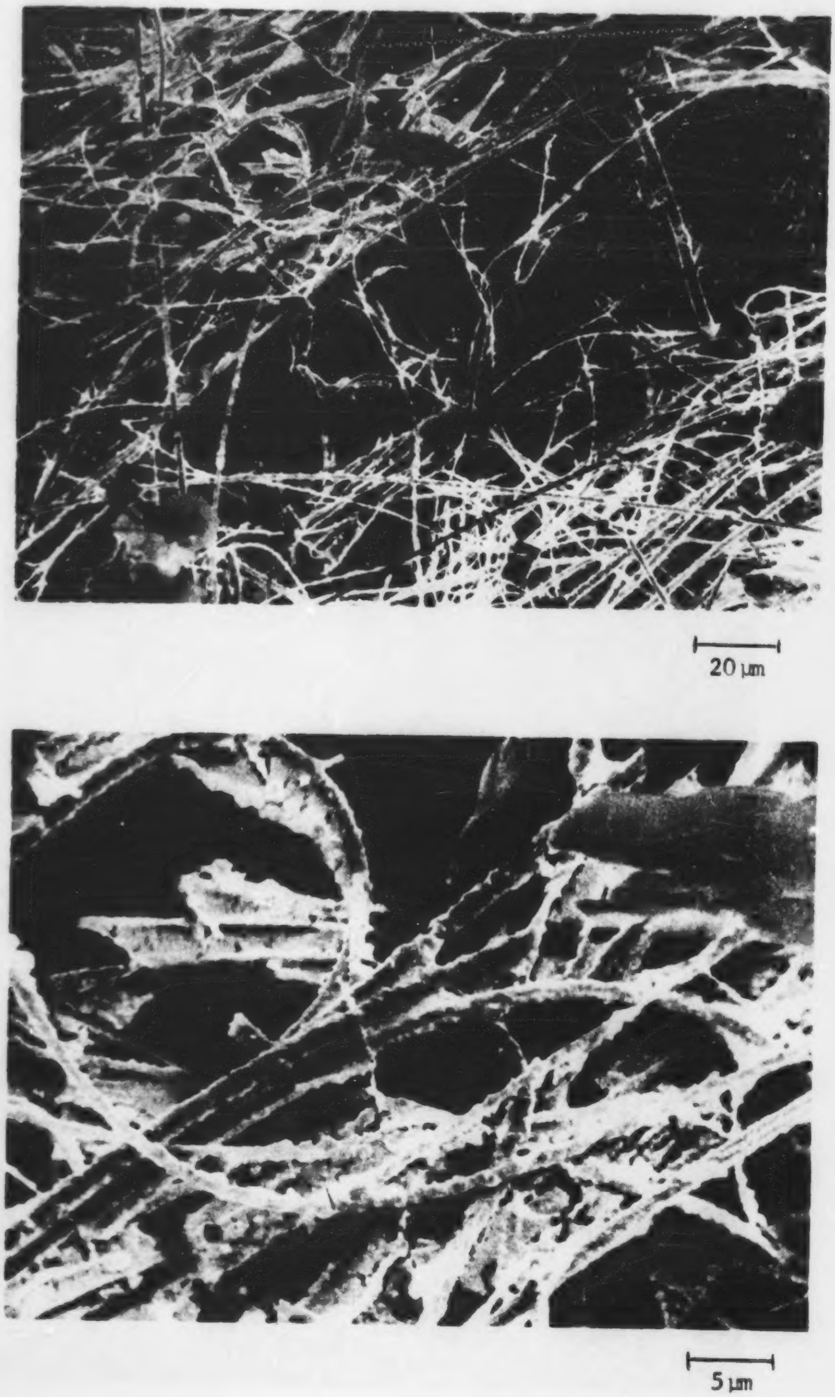
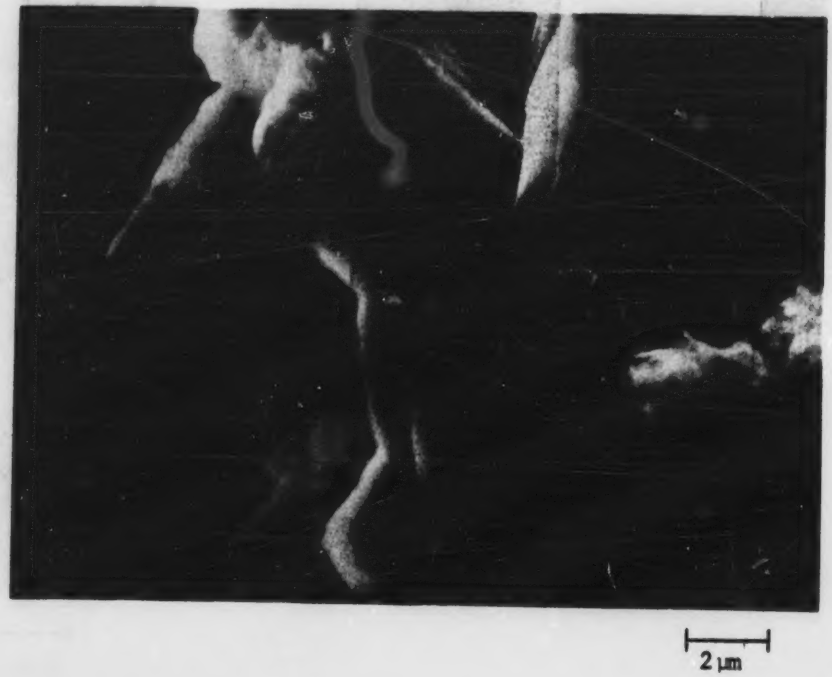
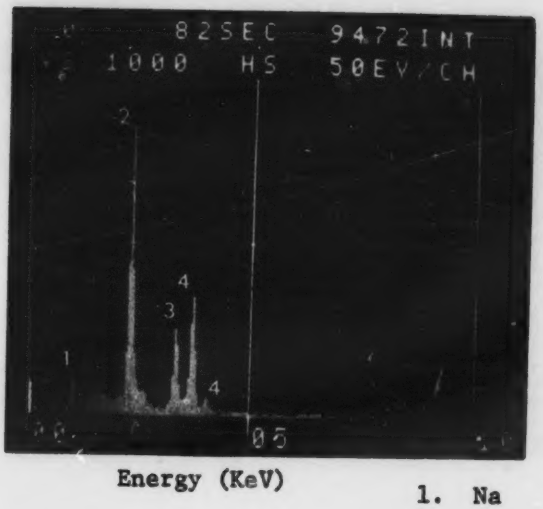


FIGURE H-2 Particulate Collected on Glass Fiber Filter, Sample NI-17A





Chemical Analysis

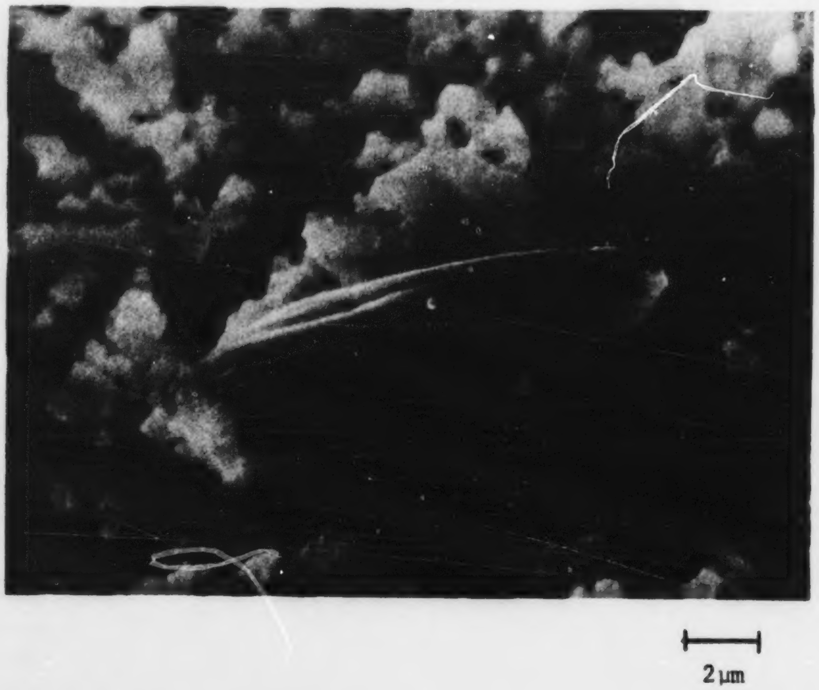
Strong - S

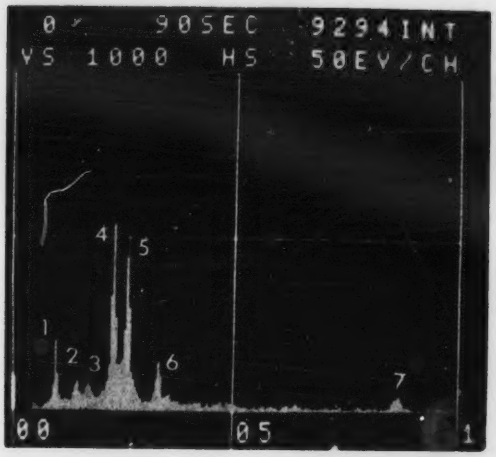
Medium - K, Ca

Weak - Na

1. Na
2. S
3. K
4. Ca

FIGURE H-3 Particulate on Organic Membrane Filter Exhibiting High Degree of Morphology and Corresponding X-ray Analysis, Sample NI-48





Energy (KeV)

1. Na 4. S
2. Al 5. Cl
3. Si 6. K
7. Zn

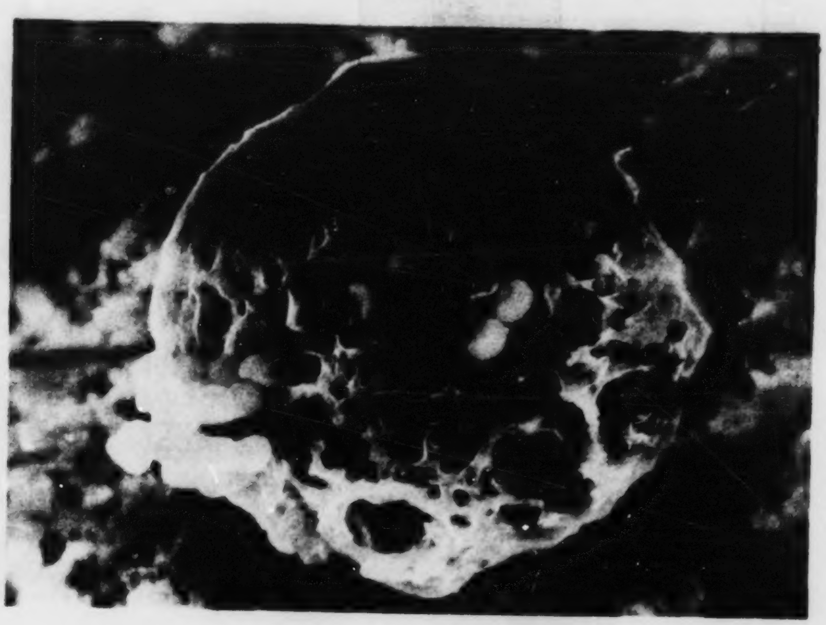
Chemical Analysis

Strong - S, Cl

Medium - Na, K

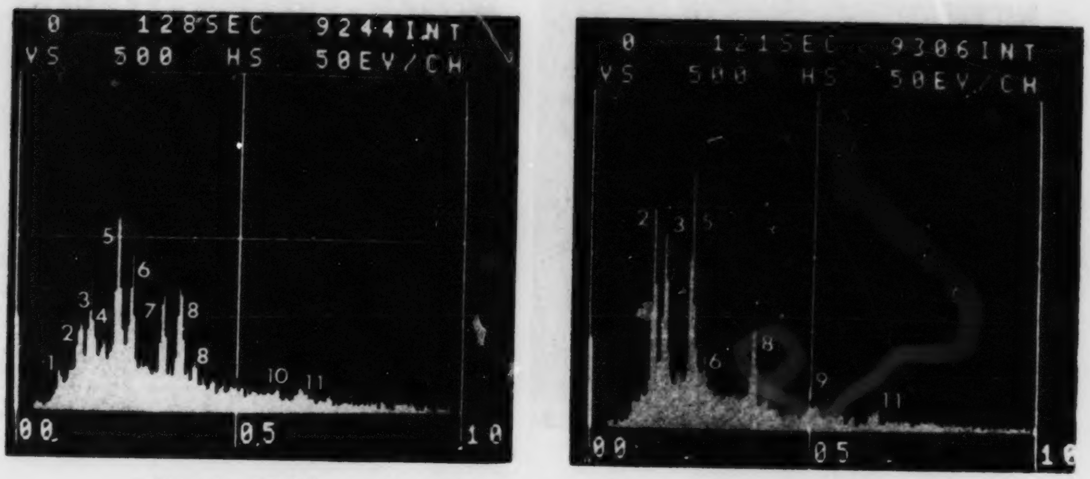
Weak - Al, Si, Zn

FIGURE H-4 Particulate on Organic Membrane Filter, Similar to Figure G-3, with Corresponding X-ray Analysis, Sample NI-48



Slag Particle

10 µm



Energy (KeV)

Energy (KeV)

1. Na
2. Al
3. Si
4. P
5. S
6. Cl
7. K
8. Ca
9. V
10. Mn
11. Fe

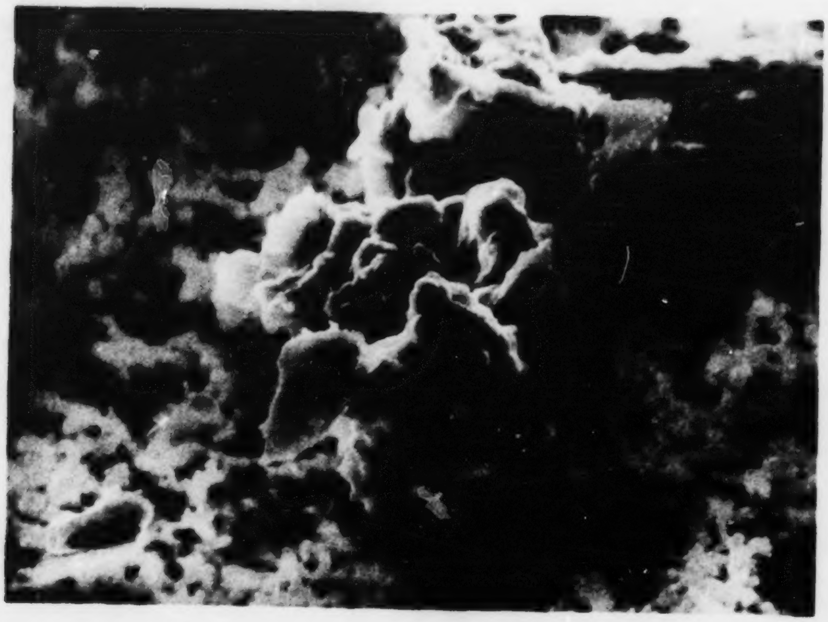
A. Small Particles

Strong - S,Cl,K,Ca
Medium - Al,Si
Weak - Na,P,Fe,Mn

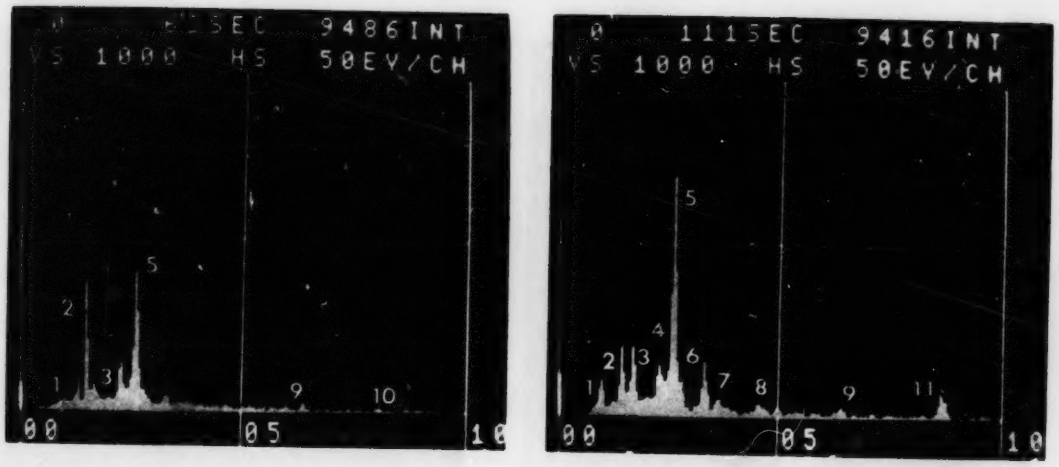
B. Large Sphere

Strong - S,Al,Si
Medium - Ca
Weak - Cl,Fe,V

FIGURE H-5 Slag Particles Collected on An Organic Membrane Filter with Corresponding Qualitative Elemental Analysis, Sample NI-60



Flyash



Area 1

Strong - Al,Cl
Medium - S
Weak - Na,Si,K,Fe,Cu

1. Na
2. Al
3. Si
4. S
5. Cl
6. K
7. Ca
8. Ti
9. Fe
10. Cu
11. Zn

Area 2

Strong - Cl
Medium - Na,Al,Si,S,K,Zn
Weak - Ca,Ti,FE

FIGURE H-6 Flyash Particle Collected on an Organic Membrane Filter with Corresponding Qualitative Elemental Analysis, Sample NI-48

APPENDIX I. SULFUR OXIDE STUDIES

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APPENDIX I

SULFUR OXIDE STUDIES

The role of sulfur oxides in the measurement of particulates is a major issue which received attention during this program and continues to deserve further study. As noted in Appendix F, not only were measurable quantities of sulfate found in the filter catch, but also much of the impinger catch was sulfuric acid. If the sulfate were simply the result of scrubbing sulfur trioxide, then it could well fit into present approach of inclusion as particulate. However, if the sulfate was due to the oxidation of sulfur dioxide during passage through the sampling train or in sample handling or treatments, the acid sulfate should not be classified as particulate.

I. FIELD MEASUREMENTS OF SO_x Levels

As given in Appendix A, literature values for sulfur oxide levels in the emissions from municipal incinerators range from 30 to 60 ppm. In order to aid us in understanding the fate of sulfur oxides in the sampling train, direct measurements of sulfur oxide levels were made. To do this, SO_3 was collected using a controlled temperature condensation technique while SO_2 was collected using an aqueous hydrogen peroxide scrubber. Analysis for collected sulfate was made using a barium ion (thorin indicator) titration procedure. The results of these measurements, made on three separate days, are given in Table I-1. It can be seen that the sulfur levels in the incinerator emissions changed from August to November, primarily as a result of increased SO_2. The latter measurements at 20-30 ppm SO_x are more consistent with earlier published results.

II. LABORATORY STUDIES

The components of the sampling train and the places where reactions of sulfur oxides might occur are described in Table I-2. The purpose of this laboratory study was to try and sort out which of these reactions might be important.

A. Reactions in the Impingers

Initial experiments examining the reactivity of SO_2 in various water solutions were carried out by conducting studies at room temperature using the apparatus schematically depicted in Figure I-1.

Air at 37 ℓ/min was passed through a water saturater and mixed with a stream of 1.5 ℓ/min of 940 ppm of SO_2 in nitrogen so that a final concentration of 37 ppm SO_2 was bubbled through 200 ml of the solution under

TABLE I-1

SO_x Levels in Incinerator Emissions

Date	Levels of SO_x (ppm)			Ratio
	SO_2	SO_3	SO_x	SO_3/SO_4
8/71	5	2	7	.25
	5	2	7	.3
	1		2	.5
	0.5	0.8	1.3	.7
	1	0.2	1.2	.2
	1	2	3	.7
	1	2	3	.7
Average	1	1.3	.34	.5
9/71	2.7	0.6	3.3	.2
	6.8	0.5	7.3	.1
	0.7	0.3	1.0	.3
	0.5	0.4	0.9	.4
Average	2.7	0.5	3.2	.25
12/8-71	26	2	28	0.1
	21	1.6	22.6	<0.1
	16	4	20	0.2
	15	2	17	0.1
Average	20	2.5	22	0.1

TABLE I-2

Possible Fate of Sulfur Compounds in the EPA Sampling Train

Sampling Train Component	Gaseous Species	Possible Reactions	Fate of Sulfur Compound	Influence on Particulate Measurement
Probe/Cyclone/Filter	SO_2	a) $SO_2+H_2O \xrightarrow{250°F} SO_3$	See SO_3 Reactions	See SO_3
		b) SO_2+particulate ⟶ Sulfites	Trapped as Particulate	Increase Weight
	SO_3	c) SO_3 Condensation	Trapped as Particulate	Increase Weight
		d) $SO_3+H_2O \longrightarrow H_2SO_4$	Condensation or Absorption	Increase Weight
		e) SO_3+particulate ⟶ Sulfates	Trapped as Particulate	Increase Weight
Impinger	SO_2	f) $SO_2+H_2O \longrightarrow H_2SO_3$	Collected as Soluble SO_2 then:	
			a) oxidized ⟶ sulfate b) volatilizes from liquid	Increased Weight No effect
		g) $SO_2+O_2 \longrightarrow SO_4$	Trapped as Particulate	Increase Weight
		h) SO_2+cations ⟶ Sulfites	Trapped as Particulate	Increase Weight
	SO_3	i) $SO_3+H_2O \longrightarrow H_2SO_4$	Trapped as Particulate	Increase Weight

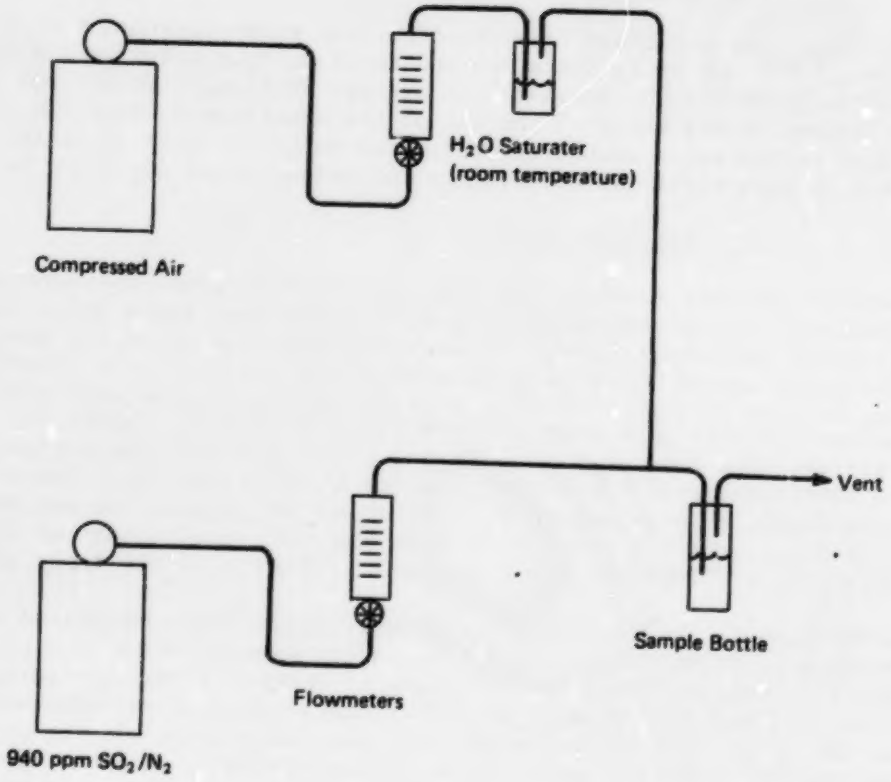
Compressed Air
H_2O Saturater
(room temperature)
Vent
Sample Bottle
Flowmeters
940 ppm SO_2/N_2

FIGURE I-1: APPARATUS FOR SO_2 SOLUTION REACTIVITY STUDIES

study for 1 hour at a total flow rate (38.5 ℓ/m, 1.36 cfm). This flow was comparable to that actually used in operating the EPA sampling train, but the concentration of SO_2 was approximately 10 times higher than any concentrations of SO_x which we had observed at the incinerator and thus represented an extreme test of the possibility that solution reactions were contributing to the high sulfate values. The observed results (listed in Table I-3) were:

1. Distilled Water

The resulting solutions from the distilled water experiment were analyzed for soluble SO_2 by I_2 titration and total sulfate gravimetrically, after oxidation of the SO_2 bromine. An average of 40 mg/ℓ of SO_2 remained dissolved in the water at the end of the experiment. This was about equal to the total amount of sulfur (as sulfate) observed in the solution so that there was no evidence for oxidation of SO_2 prior to analysis.

2. Impinger Catch

Several impinger catches from the reciprocating grate incinerator were combined to give sufficient sample for study (see Table I-3). After dividing into three parts, two portions were treated in the same way as the water sample above, and one portion was analyzed as a control (no SO_2 bubbled through). On the average, the SO_2 treated solutions contained slightly more sulfur oxides than the control. Since the results were the same when measuring SO_2 and total sulfates, the differences can be attributed entirely to the presence of dissolved SO_2. Therefore, once again, a large amount of sulfate was not formed from the SO_2 in the impinger. It is interesting to note the much lower amount of SO_2 dissolved in the impinger solution--undoubtedly due to the lower pH (2.5).

A final study was carried out with a different set of combined impinger catches by treating them initially in the same manner as the previous set, but then concentrating the solutions to about 5 ml and analyzing for total sulfate (see Table I-3). The purpose of this exercise was to see if the additional concentration step and temperature effects encountered in the EPA procedure would result in conversion to sulfate. The two SO_2 treated samples showed an average 5-6 mg/ℓ greater $SO_4^=$ value than the control samples. This would only amount to 2-3 mg in a typical 300-500 ml impinger catch which was equivalent to 10-15% of the impinger sulfate catch.

In summary, it did not appear that the solution conversion of SO_2 to $SO_4^=$ can account for more than 10-20% of the observed impinger catch sulfate values. Junge and Ryan (Quart. J. Roy. Meterol. Soc., 84 46 (1956)) showed that SO_2 was not oxidized in water, but that conversion to sulfate could proceed at pH's greater than 3 in the presence of transition metals such as Mn, Cu, Fe, and Co (which effectiveness decreased in the order listed). At a pH of 3 the oxidation proceeds at half the rate that it does at pH 4 and above, and it is completely stopped at a pH of 2. Since the impinger solutions rapidly reach a pH of 2.5 due to the collected HCl, it was not surprising that we did not observe SO_2 oxidation in impinger solutions.

TABLE I-3

Analysis Results from SO_2 Solution Studies

		Soluble* SO_2 (mg/ℓ)			Total SO_x** as SO_4 (mg/ℓ)	
Sample	**Treatment**		**Ave.**	**As SO_4**		**Ave.**
Distilled Water	SO_2 treated	33	40	60	54	61
		48			68	
Impinger Catch	SO_2 treated	10	9.5	14	48	50
		9			52	
	Control (no added SO_2)	6	6	9	47	47
Impinger Catch	Evaporated to 5ml	--			12	10
	Evaporated to 5ml	--			7	
	Control, no added SO_2	--			5	4
	Control, no added SO_2	--			3	

*Via titration with iodine.

**Oxidation and precipitation as $BaSO_4$.

B. Oxidation of SO_2 by the Filter

In order to test the possibility that oxidation of SO_2 by the filter and subsequent scrubbing of the resultant SO_3 by the impingers could account for the sulfate in the impingers, two different experimental approaches were employed. In the first, air was bubbled through water and then joined with a sulfur dioxide in nitrogen (940 ppm) stream in the proper proportions to give a final gas mixture containing 45 ppm SO_2 flowing at 0.5 CFM. This gas mixture was passed through a preheated stainless coil (1/4 in. O.D. x 20 ft) and then through a metal filter holder containing the filter to be studied, both contained in an oven maintained at 250°F. The exit gas stream was then bubbled through an impinger containing 200 ml of 80% isopropyl alcohol cooled in an ice water bath (see Figure I-2a). Following the one-hour run, the impinger solution was warmed to room temperature and air bubbled through it for ten minutes to remove most of the dissolved SO_2. The results of these tests using filters collected during the incinerator sampling, as well as a blank, are given in Table I-4. It is clear from this data that not very much SO_3 was collected in the isopropanol impinger, nor were measurable amounts of sulfate being formed on the filter, based on the change in weight data. Based on this data, for a standard 60 SCF sample, possibly 2-3 mg sulfate would be collected by the impingers due to filter catalysis from 45 ppm SO_2 gas stream. We assume that even lesser amounts would result from a 5 ppm stream. To ensure that SO_2 was in the gas stream at the desired levels, one run was made with an impinger containing hydrogen peroxide scrubbing solution. Roughly 95% of the calculated SO_2 for a 45 ppm stream was recovered as sulfate in the impinger, confirming that the SO_2 was present as planned.

Because of the lack of evidence for SO_3 in the impinger from the above experiment, we were concerned about the possibility that either the metal filter holder may have reacted with the SO_3, or the isopropanol impinger was very inefficient and low SO_3 recoveries were obtained. To study the possibility that the metal system and isopropanol impingers had an effect, a second set of experiments were performed using the same gas mixture and preheating system but then passing this mixture into the heated all-glass filter holder on the RAC sampling train. Flows were maintained at 0.5 CFM for one hour for each run and scrubbing was accomplished via the use of the normal three impingers arrangement in the RAC train (water at ice bath temperatures). Schematic representation is shown in Figure I-2b. The results of these experiments are given in Table I-5. In this case, there are two runs whereby significant quantities of sulfate were found. The reason for not finding much sulfate in the other two runs is not clear. Possibly, the system needed equilibration to overcome initial buildup of SO_3, or else some unknown variable was out of control.

TABLE I-4

Results from First SO_2 Filter Oxidation Study

Filter			Found (mg) in the Isopropanol Impinger		
Code (NI-)	Degree of Loading (mg)[a]	Loss in Weight (mg)	Soluble[b] SO_2	Total SO_x[c] as SO_4	Average[d]
--	Blank	-2.5	0.1	1.4	
--	Blank	-3.4	0.5	1.3	0.8
--	Blank	-4.1	---	1.1	
74-1	293	-12.2	---	1.0	
28-1	231	-4.6	---	0.9	0.4
13-1	246	-2.2	---	1.1	
80-1	108	-6.4	---	1.9	1.1

[a] Each filter lost weight during the run.
[b] Analysis: titration with iodine.
[c] Analysis: Oxidation and precipitation as $BaSO_4$
[d] Corrected for 0.5 mg sulfate blank due to soluble SO_2.

TABLE I-5

Results from Second SO_2 Oxidation Study

Filter		Found in Impingers (mg)*			
Code	Loading	SO_2	Total SO_x	SO_4 due to SO_3+	Average
--	Blank	0.3	8	5	4
--	Blank	0.5	6	3	
24-1	870	0.5	7	4	5
46-1	436	0.5	8	5	
78-1	153	0.5	25	22	21
14-1	237	0.3	22	19	

*Impinger solutions (210-230 ml) boiled and evaporated to less than 200 ml and then diluted to 200 ml for analysis.

+Included rough correction for residual SO_2 and 2 mg SO_4 due to oxidation.

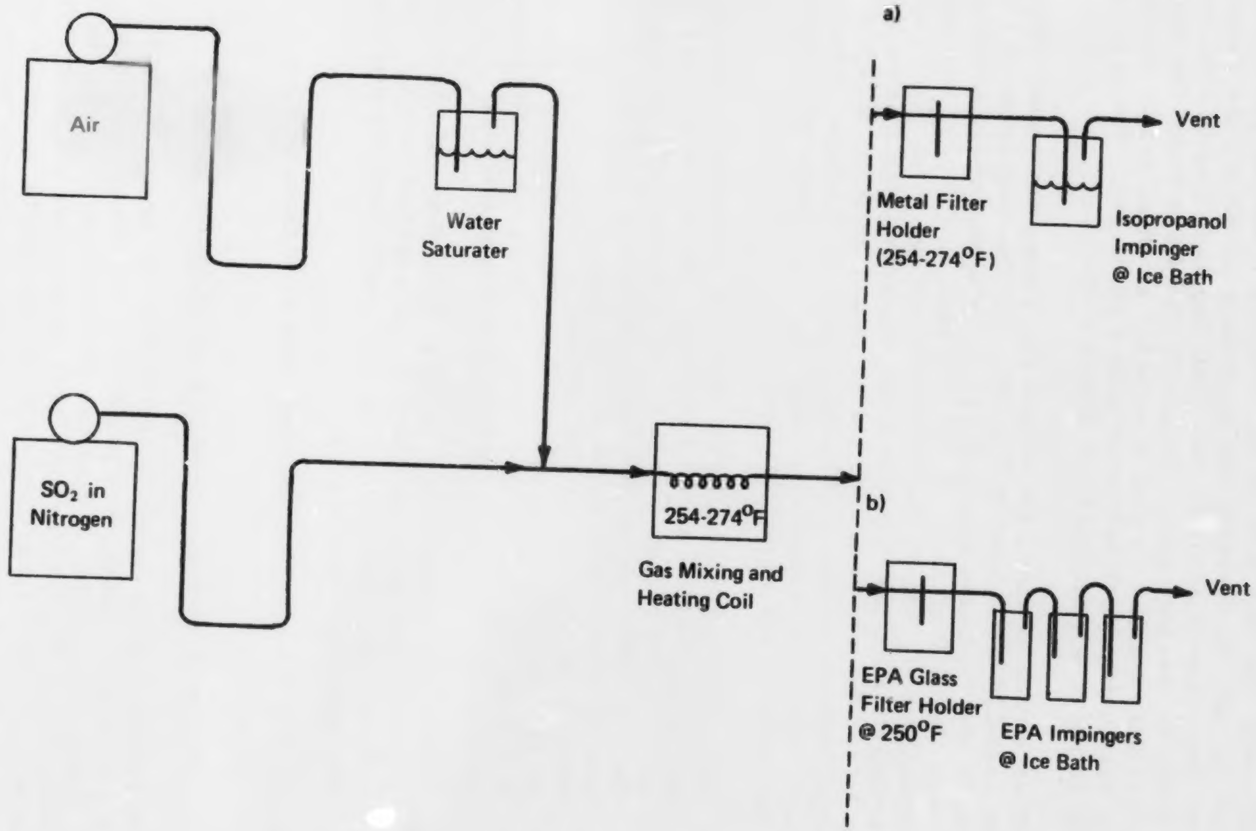
Air
SO_2 in Nitrogen
Water Saturater
254-274°F
Gas Mixing and Heating Coil
a)
Metal Filter Holder (254-274°F)
Isopropanol Impinger @ Ice Bath
Vent
b)
EPA Glass Filter Holder @ 250°F
EPA Impingers @ Ice Bath
Vent

FIGURE I-2: SCHEMATIC OF APPARATUS EMPLOYED FOR SO_2/SO_3 OXIDATION STUDIES

Because the results of these experiments were contradictory, further work was performed. In order to avoid potential problems of SO_3 adsorption on metal, this work was done with an RAC sampling train all glass system (from the filter on) and, to decrease the solubility of SO_2 in the collection system and more closely simulate the final impinger composition, we switched to 0.01 N HCl in the impingers. In actual field practice, the impinger becomes acid very quickly so that a solution at pH of 2-3 is probably more realistic than using distilled water with a pH of 5-7. The apparatus for this work is shown schematically in Figure I-2b.

In the first series of runs, the 45 ppm SO_2 stream was passed through the RAC train assembly for 1 hour at 0.5 CFM. At the completion of the run, the water in the impingers was combined and evaporated via heating at about 90°C to less than 200 ml and then diluted back to 200 ml. Portions were then analyzed for SO_2 via iodine titration and for total SO_2 by means of precipitation with barium chloride after oxidation with bromine (see series A, Table I-6). For the second series of tests, Series B in Table I-6, the experimental runs were duplicated except that the impinger solutions were analyzed directly rather than after an evaporation and a concentration step. Conclusions from these runs were:

- Large quantities of sulfate were not collected in the impinger--by any mechanism--when a 45 ppm SO_2 gas stream was passed over a heated glass filter system at 250°F for as long as four hours. Our experiments have shown that between 3 and 6 mg of sulfate was collected; this would account for, at most, 10-30% of the total sulfate found in the impinger solutions of a test run at an incinerator. (The precision of these analyses is probably such that the differences shown in Table I-6 between series A and B, should not be considered very significant.)
- Most of the sulfate may, in fact, have been soluble SO_2--not SO_3 collected by or produced in the impinger so that, it may be that the SO_4 was produced by the sample handling procedures in the analytical methodology.
- No differences were observed with or without a glass filter in the system.

C. Influence of Sample Handling on Oxidation of SO_2

To learn how the sample handling influences the levels of sulfate found, another set of experiments were performed. In these, unheated SO_2 in air at two levels (45 ppm and 10 ppm) was bubbled directly into the impingers containing 0.01 N HCl (at ice bath temperature) for one hour. The water samples were analyzed immediately for SO_2 via iodine titration and then evaporated to 5-10 ml and analyzed for total sulfate via barium precipitation. The purpose of this test was to see how much SO_2 is lost during evaporation and to examine the effect of SO_2 concentration in the gas stream. The results of this study (see Table I-7) confirm that:

TABLE I-6

SO_2 Filter Oxidation Studies

Sample Conditions		Found in Impingers (mg)		
			SO_2[c]	
Series[a]	Filter Used[b]	as SO_2	$SO_4^{=}$ Equivalent	Total Measured SO_4[d]
A	None	0.4	0.6	4.0
	Blank	0.5	0.8	5.4
	NI-24-1	0.3	0.5	4.3
	NI-14-1	0.3	0.5	5.1
				Average = 4.7
B	None	4.6	6.9	6.4
	Blank	3.8	5.7	5.7
	NI-24-1	3.6	5.4	5.6
	NI-14-1	2.9	4.4	4.8
				Average = 5.6

a - Series A - Impinger water partially concentrated before analyses.
Series B - Analyzed directly.

b - Filter obtained via sampling run as indicated in Appendix D, Tables D-2 and D-3.

c - SO_2 determined by iodine titration and then sulfate equivalent calculated.

d - Sulfate determined gravimetrically after oxidation with bromine.

TABLE I-7

SO_2 Analysis Studies

SO_2 Level in Gas[a] (ppm)	Found in Impingers (mg)			
	SO_2 Levels[b]			
	SO_2	Sulfate Equiv.	Sulfate after Evaporation[c]	Average
45	2.1	3.2	3.8	4.7
45	3.3	4.9	4.4	
45	3.6	5.4	2.7	
45	5.1	7.6	7.9	
10	1.6	2.4	4.9*	1.6
10	0.7	1.1	1.6	
10	1.1	1.7	1.9	
10	1.1	1.7	1.3	

a - Estimated from flow rates.

b - SO_2 determined via iodine titration and sulfate equivalent calculated.

c - Impinger solutions evaporated to 5-10 ml and then total SO_x determined gravimetrically after oxidation with bromine.

* - Not included in average, if did the average would be 2.4 and conclusion essentially the same.

- Most of the SO_2 solubilized in the impingers at the end of the sampling run remained available to be measured as sulfate even after concentration of the impinger solution to a few ml. Therefore, to explain the low loss of SO_2 during evaporation, most of the SO_2 must have been oxidized fairly rapidly during the evaporation step.

- The level of SO_2 in the gas stream had an influence on the SO_2 dissolved and thus the residual sulfate found in the impingers (higher SO_2 leads to higher sulfate). Thus the 45 ppm stream gave the same results as in Table I-6. However, with less SO_2 in the gas stream, the 10 ppm stream caused less to be absorbed by the solution.

- The amount of sulfate generated in the impingers due to SO_2 solubilization will probably be low when the EPA train is used for incinerator testing--because the SO_2 levels in the gas stream tend to be low.

D. Combined Field and Laboratory Tests

To aid in our understanding of what happens to sulfur oxides in the sampling system, we performed a field test whereby the sulfur oxide levels were measured at the same time as samples were taken using the EPA sampling train. Because it was operationally easier, we used two complete sampling systems with the nozzles directly adjacent to each other in the stack. Our assumption was that serious concentration differences within a one-foot area in the gas stream, although possible, were not likely. SO_3 and SO_2 were collected separately via a controlled condensation collector and a peroxide impinger respectively. (The resultant sulfate was determined by the conventional barium titration procedure with thorin indicator.) Sulfur dioxide and sulfate levels in the EPA train impinger solutions were determined by iodine titration and barium precipitation respectively. The results of these experiments are given in Table I-8 and they led to some interesting observations:

- The amount of sulfate in the impingers did not correlate with the measured levels of SO_3 in the incinerator effluent.

- The collection of total SO_x in the impingers was about 35% except for one case of 90%.

Developing a clear explanation of these results is not easy. The high variability of the measurement of SO_3 at these low levels using the controlled temperature condensation technique is one possibility. Thus, maybe the SO_3 results are in error and the gas stream really had more SO_3--enough to account for what was found in the impingers. This certainly could be the case for NI-86,87 and 88. However, it is an unlikely explanation for NI-85. Either that run was a fluke or oxidation of SO_2 must have occurred early in the sampling train and the

TABLE I-8

Determination of Sulfur Oxide Levels in Incinerator Effluents and Impinger Solutions

Sample No.	Concentration in Stack Gas (ppm)[a]		Sample Volume (m^3)	Calculated Available Sulfate[b] (mg)			Measured Sulfur Oxides in Impinger[c]			Percent SO_x Found in Impingers
	SO_2	SO_3		SO_2 and SO_4	SO_3 as SO_4	Total	SO_2[d]	SO_4[e]	Total	
NI-85	26	2	1.3	142	11	153	1	139	140	90
NI-86	21	1.6	1.4	120	9	129	8	38	46	33
NI-87	16	4	1.3	84	21	105	7	28	35	33
NI-88	15	2	1.5	95	13	108	7	32	39	35

a - Determined on separate gas sample collected at same time as EPA sample and close to same sampling location.

b - Calculated based on SO_2 level and volume sampled (1 ppm SO_2 represents 4.2 mg sulfate per m^3 sampled).

c - Collected via standard EPA sampling procedure.

d - Determined by titration with iodine.

resultant SO_3 collected in the impingers. (We could not make this happen in the laboratory but possibly field conditions were different.)

In an effort to help explain this dilemma, an experiment was performed whereby an SO_2 containing gas stream was bubbled through impinger solution collected at an incinerator in another attempt to generate significant amounts of sulfate in the sampling train in the laboratory. The experimental procedure was similar to earlier work except that an effort was made to utilize extreme conditions in the hope of generating some sulfate. Thus, for this work, we used a 45 ppm SO_2 in nitrogen gas stream and the setup shown in Figure I-2b.

The gas stream, where temperature varied from 206-318°F, was passed at a flow rate of 0.6 cfm for 4.7 hours over a filter previously used in the field (Run No. NI-14) at 250°F, and through impinger solution from Run No. NI-88. After determining the SO_2 and sulfate levels in the original impinger solution, at the end of this run, the impinger solution was re-analyzed for sulfate and residual SO_2. The results were:

	Amount Found (mg)		Sulfate Corrected for SO_2
	Sulfate	Residual SO_2	
After	48	13	35
Before	32	11	21
Difference	16		14

Looking at either the corrected or uncorrected (for residual SO_2) sulfate values, it would appear that a little sulfate (14-16 mg) did build up in the impinger solution. However, when it is recognized that the total SO_2 passed through this solution represented roughly 900 mg of sulfate, it can be seen that the sulfate pickup in the impinger was not very significant. Thus, we have been unable to duplicate conditions in the laboratory whereby appreciable sulfate is collected in the impingers due to oxidation of SO_2 by the filter, filter holder or impingers.

E. Distribution of Sulfate in Sampling System

A presentation of the distribution of sulfate between the various parts of the sampling train for the four runs used for thorough quantitative measurement is given in Table I-9. As can be seen from this data, the sulfate was fairly evenly distributed between the probe/cyclone, filter and impingers--but on the average more in the latter. Whether all of the measured sulfate was due to SO_3 and SO_2 or includes solid sulfates collected on the filter and probe in unknown.

TABLE I-9

Distribution of Sulfate in Sampling Train

Sample (NI-)	Distribution of Sulfate (%)			Total Weight Found (mg)
	Probe/Cyclone	Filter	Impinger	
77	28	40	32	70
78	16	42	42	103
79	28	34	38	93
80	28	26	46	61
Average	25	35	45	82

III. VAPOR PRESSURE DATA FOR SO_3

The dew point of small amounts of SO_3 in the presence of excess amounts of water vapor has been predicted from theoretical thermodynamic calculation by Muller[2] and confirmed experimentally by Lisle and Sensenbaugh[3].

From this work, the relationship between SO_3 concentration and temperature is:

Temp. (°F)	SO_3 (ppm)
230	0.4
250	2
270	9

In the average sample taken for this program, one ppm SO_3 represents 6.5 mg sulfate.

IV. DISCUSSION

It has always been clear that SO_3 will be collected by the sampling train in one way or another--the only question has been where. Our best estimate at this time is that, due to vapor pressure limitation, no more than 10-15 mg of sulfate in our "standard catch" can be attributed to SO_3 originally in the gas stream. This assumes a 2 ppm vapor pressure for SO_3 at a filter temperature of 250°F (the actual temperature has varied from 210-270°F). During all of our experimental field measurements, the measured SO_3 level has been above 2 ppm only once (4 ppm), so that a 10-15 mg maximum probably is real. Because of its high reactivity, most, if not all, of the SO_3 probably reacts with materials on the filter or probe and never reaches the impingers. In any case, this amount of sulfate added to the filter is a relatively small percentage (5-10% of the total 150-250 mg) so that the question as to whether the sulfate on the filter (or probe and cyclone) came from SO_3, SO_2, or particulate sulfate is not too important for incinerator effluents.

Our laboratory results do not support the hypothesis that the filter at 250°F or the impingers themselves will convert significant quantities of SO_2 to SO_3 or sulfate. Thus, even in the most extreme case, very little sulfate was formed during passage of SO_2 over a hot filter or through an acidified solution. This was true even though we employed metal or glass filter holders, clean glass filters or filters which contained particulate catch from an incinerator. Even though the impingers contain practically no mineral ash, it may be that the actual impinger solution acts as a catalyst in a way that we have not duplicated in the laboratory. Another possible alternative is that the probe, which is generally hotter than 250°F acts as the catalyst for the oxidation. This is the only portion of the sampling train that was not duplicated in the laboratory.

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[2] "A Contribution to the Problem of the Action of Sulfuric Acid on the Dew Point Temperature of Flue Gases." P. Muller, Chem. Ing. Tech., 28, 279, (1956).

[3] "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases." E.S. Lisle and J.D. Sensenbaugh, Combustion, 36 (7), January, 1965.

APPENDIX J. SOME IMPORTANT CONSIDERATIONS FOR SAMPLING OF PARTICULATES

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APPENDIX J

SOME IMPORTANT CONSIDERATIONS FOR SAMPLING OF PARTICULATES

I. INTRODUCTION

This chapter will focus on the needs and problems associated with source factors and equipment used in characterizing particulate matter. Our intent in doing this is to clearly delineate objectives and goals associated with the determination of particulate loadings, the pitfalls that one may encounter by the use of various pieces of sampling equipment, and the tradeoffs that are available when deciding to use one device rather than another. In addition, this discussion will serve as a backgound for the specific evaluations of individual methods which was given in Appendix C.

Throughout this discussion it is important to remember that the basic objective in measuring particulate concentrations in the emissions from incinerators is to answer such questions as:

- Is the combustion process generating large quantities of particulate matter?
- How effective are the Air Pollution Control devices?
- What amount of particulate matter is being emitted to the atmosphere?

A major problem in attempting to answer these questions is defining the term particulate. Does it include only inorganic solids that are stable at high temperature? hydrates? anything that will condense upon leaving the stack? If condensibles are to be included, then how far from the stack can condensation occur and what temperatures are relevant? Such considerations serve to illustrate that the definition of particulate matter has a great influence on what methodology which can be considered. Traditionally, interest has been in the mass of dust emitted which contributed to dust fall (solid particles in the gas stream >1/μm). At the present time there is interest in many other effects of air pollution and, as such, the size spectrum is widened. Cloud formation in the atmosphere is related to nuclei population; atmospheric visibility and haze are related to strong scatterers (0.1 to 1 μm); toxicity is frequently interpreted in terms of a "respirable" fraction (approximately 0.1 to 5 μm); the mass of material emitted to the atmosphere is in the larger sizes (> 1μm).

Specific reference to sampling protocol or recommendation of specific equipment has been deliberately omitted. Methods for testing incinerators have been published in the Federal Register, December 23, 1971 and provide complete detailed descriptions of an acceptable methodology. The sections which follow will permit the reader to appreciate the many considerations inherent in the specification and use of the Federal Register methods.

II. TESTING AN INCINERATOR

A. Pretest Planning

Pretest planning considers the objectives of the test against the nature of the operation under study. Such factors as steady-state vs. transient operation, lengths of cycles, peak periods of emission, estimated gas composition and pollutant concentrations, gas temperature and pressure, duct size, gas velocity and humidity are examined to select an appropriate collection method, method of analysis, sampling rate, sampling interval, number of tests required for proper statistical analysis, as well as to consider less obvious needs, such as special materials of construction (temperature or corrosion effects, etc.). Such mundane factors as availability of ladders, scaffolding, sampling ports, lighting (for night work), and coordination with operating personnel must be included in the test plan.

Adequate planning increases the probability for representativeness of the sample which is the real measure of success in the tests to follow.

The alternative to pretest planning is the too familiar trial-and-error method which leads to extended experimental programs, overlooked key data, and a generally more costly and less representative result.

B. Source Factors

Incinerator sources must be examined to evaluate those operational and configurational parameters which influence the sampling process or are needed to complete test computation. These factors include:

Flue gas temperature
Pressure
Flow velocity
Uniformity of flow, - gross geometry, bends, length
Flue size - cross sectional geometry
Flue gas composition and water content
Process parameters - e.g., for combustion, excess air, rate, type of firing, firing rate, waste composition (heat content)
Control devices
Working conditions

The relationship of each factor or its influence on sampling configuration or procedure is discussed below.

1. Flue Gas Temperature

The temperature at the sampling point determines whether condensibles are sampled as gases or particles. This obviously influences the choice of sample train components and probe temperature (heated or cooled) and the choice of materials of construction. Temperature also influences gas density and must be considered in velocity and mass flow calculations.

2. Pressure

Pressure at the sampling point determines (with temperature and composition) the density of flue gas and is reflected in the correction factors needed to convert measured values to standard conditions.

3. Velocity

Velocity is, like temperature, a very important parameter. It is necessary to know velocity to select a proper size probe and also to adjust the sampling flow rate for isokinetic conditions (necessary to eliminate sampling errors at the inlet). Calculations of emission rate are based on velocity traverses and flue area.

The selection of an instrument to measure velocity will depend on the magnitude. For the velocities characteristic of many large installations (velocity > 10 ft/sec), pitot tube measurements are most generally made. Pitot tubes with included monometers are not sufficiently accurate for velocities much below this value and alternative methods are used.

4. Uniformity of Flow

Closely related to the magnitude of velocity is its uniformity

- Across the sampling plane
- As a function of time at a given point.

The spatial uniformity depends primarily on the configuration of the flue, duct, chamber or whatever conduit containing the effluent is being sampled. There is perhaps more variability in this factor than in any other. Every large installation is more or less unique. One is generally advised to sample several diameters downstream and a few diameters upstream of any flow disturbing element. In practice it is rare to find an ideal location.

Temporal uniformity depends upon the type of operation (batch or continuous) and is very important in sampling.

5. Flue Size

The dimensions of flue or duct determine the number of samples that must be taken across the sampling plane to obtain a representative measure. Small rectangular ducts require fewer measurements to obtain the same degree of accuracy as large ducts. Accuracy for a given number of points is not a function of size for circular ducts. Interference produced by the introduction of the sample probe may be a factor in small units.

6. Gas Composition and Water Content

Gas composition must be known to completely characterize gas flow and thus the total emission. In the case of combustion effluents, composition data are also needed to correct the measured values for particulate loading to some normalized basis, e.g., 12% CO_2, 50% excess air. Water content (dew point) must also be considered to prevent condensation before particle collection. Condensation can lead to plugging of the collector and/or wetting of the sample.

7. Process Parameters - e.g., Incineration Processes - Excess Air, Waste Composition, Heat Content, Type of Firing, Load

Data on these factors is needed to provide a complete record of the conditions present when the test is made. Type of waste, method of firing, and load are major determinants in the type and magnitude of emissions. During startup or load changes, excessive emissions can be produced.

8. Control Devices

The application of any control devices will change both the total loading and particle size distribution in an effluent stream. Tests on units with high efficiency collectors sometimes require different sampling configurations or test procedures at the inlet and outlet due to the large reduction in loading. Furthermore, many dry collectors operate at elevated temperatures and would have little or no effect on condensibles.

Wet scrubbers introduce a different type of problem. The effluent is cooled, saturated, and often loaded with liquid water. Means to separate the water and prevent filter plugging are required.

9. Working Conditions

Difficulties and hazards result from the necessity of working on poorly accessible, often elevated, poorly lighted, cramped platforms in all weather conditions. Also, size, weight, fragility, reliability of the sampling system, long duration of sampling test program, and distance of sampling team from home base are practical factors that will be of utmost importance. In spite of these hardships, it is essential that capable and experienced personnel be directly involved in the field test program.

C. The Sampling and Collection Train

In this section, the individual components normally associated with sampling and collection of particulates will be discussed. The basic reason for setting up and utilizing a sampling train is to obtain a sample that is "representative" of that in the original environment. As discussed in Section B above, meeting this objective is dependent on a wide range of factors. Within the context of this program, we aimed for all matter which would be a particle or condensible at 70°F. Therefore, as the individual sampling train components are discussed, they must be viewed in the light of this very specific definition.

The apparatus used for the sampling of all stationary combustion sources, including incinerators, can be divided into modular components including: sampling nozzle, probe (sometimes temperature controlled), collection device, water condenser and/or desiccant column, sample flow meter, (gas temperature, pressure and water content at the meter are essential), and air mover.

Each component is discussed below.

1. Nozzle

The first unit of a sampling system is the nozzle which is connected directly either to a probe or a collecting device. The composition of the materials used to construct nozzles is also important. Nozzles are generally made of stainless steel, and less frequently of glass or brass. Vycor glass is capable of withstanding the high temperatures but the rigors of field work suggest non-glass nozzles. Hydrofluoric acid is one of the few components in the gas stream which might affect glass but it probably is not present in the effluent in high enough concentration to be a determining factor. Brass has been used (because of ease in machining) but because of corrosion and possible reaction with sampled gases, is not considered to be appropriate. Lining the nozzle with porcelain or some other material might be considered but the material would have to be able to withstand large changes in temperature and the differential in coefficient of expansion would have to be small to prevent the lining from spalling off. In general, the use of high nickel alloy stainless steel offers the optimum in serviceability compromise. It eliminated the breakage problem and since the nozzle is short, chemical reactions with the stainless steel are minimized.

Shape of nozzle is important to sampling accuracy both in respect to providing passage for the solid particles into the sample and also the creation of turbulence in the immediate area of collection. Whiteley, and Reed(1) conducted a series of experiments on the effects of the shape of the sampling nozzle on the accuracy of sampling under isokinetic conditions. Using tubing of 5/8" O.D. and 1/2" I.D., they constructed several nozzles, each with a different angle of chamfer and tested them against the collection accuracy of a nozzle with a 15° chamfer.

A nozzle with 120° angle of chamfer showed only 0.5 percent variation in accuracy from that for the 15° angle; the 180° (flat) nozzle showed a variation of +10% in collecting both large and small particles.

In the above series of tests, the upstream or right angle projection of nozzle-probe combination was 3-5/16" long. From a subsequent series of tests it was found that the projection of the nozzle at right angles to the probe should be greater than 1-1/4" and probably should be as long as 3-5/16".

The diameter of sampling nozzles is generally predicated on other factors inherent in the sampling system. Generally the nozzle area is chosen to achieve isokinetic conditions within the pumping capability of the system for the particular stream velocity. Nozzles in a size range of 0.250 to 0.625 inches in diameter are used extensively as many sampling systems are designed to sample at a rate of approximately 1 SCFM. These sizes, coupled with the flexibility in the pumping source, are well suited to achieve isokinetic sampling conditions in most situations. Nozzles of larger size, 0.75 to +1.25 inches in diameter, have been used on systems for sampling greater volumes of gases. There are no upper limits on diameter of a nozzle other than the capability of a system to pump and handle a large volume rate of sample and the dimensions of the duct.

A minimum of 0.250 inches diameter for sample nozzles has been stipulated in ASME Power Test Codes.

A second type of nozzle which in theory is self-adjusting has been used. The so-called "null" type nozzle contains chambers surrounding the tip in which static pressure just inside and just outside the nozzle is measured. In theory when the sample flow is adjusted so that the two are equal, isokinetic conditions are achieved. In practice, significant errors are introduced by differences in flow, inside and out, surface roughness, etc. Tcynbee are Parkes(2) have developed a null probe design for which they claim almost no deviations from isokinetic flow.

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1. A.B. Whiteley and L.E. Reed, "The Effect of Probe Shape on the Accuracy of Sampling Flue Gases for Dust Control," Journal of the Inst. of Fuel, 32, pages 316-20, (1959).

2. P.A. Toynbee, W.J.S. Parkes, Intern. J. Air Water Pollution, 6, 13, (1962).

However, an extremely sensitive micromanometer is required to measure the balance of the static pressure tubes and considerable flexibility as well as very fine adjustment is needed in the suction source. Any blocking or deformity of the static holes introduces error. Null nozzles must be calibrated at approximately the temperature and velocity (Reynolds Number) at which they are to be used. In general, the null nozzle does not offer an advantage in precision or accuracy over other nozzles, and, in fact, will introduce errors through use outside of its calibrated range.

In addition, orientation of the nozzle relative to the flow lines of the gas stream is important as shown in Figure J-1. The ratio of the indicated concentration (c) and true concentration (Co) is plotted against the angle between the nozzle and the flow lines. Results for several particle sizes are shown.

Therefore, in summary, for optimum sampling, isokinetic conditions are necessary and the nozzle should be constructed of a high nickel alloy stainless steel, be between 0.25-0.6 inches in diameter, have between 15° and 120° chamfer tip, be 2-3" long and be pointed into and parallel to the gas flow.

2. Probes

Probes are of two general classes, simple and temperature controlled. Probes are frequently heated to prevent losses in sample lines through condensation. Alternatively, one can use a simple probe, but one must use very careful handling techniques and quantitatively wash condensate and precipitate from the probe and sampling lines. This material is then combined with the material in the collector. Cooled probes are used where one is sampling at temperatures above 800°F. Generally, the probe is introduced to a stack at right angles to the direction of flow. This requires a 90° bend so that the nozzle will face the nozzle into the flow. This should be a smooth 90° bend and free of burrs or imperfections. The diameter of the probe is such as to maintain transport velocity for particles and to minimize the time of contact with corrosive gases.

Stainless steel probes are available commercially and are frequently used. They have the advantages of durability, strength and ease of attachment to other components. However, stainless has the disadvantage of a high potential for reaction with sample gas--especially acids, and because of the length of the probe (frequently up to fifteen feet) minimizing corrosion is important. Reaction with the sampled gases tends to cause pitting and deterioration of the probe with increasing problems of cleaning and introduction of error.

Glass probes have been used on extremely corrosive gases and have the advantage of being relatively inert except for reaction with fluorides. Because these are not a common constituent in incinerator effluents, this may not be a service problem. Glass probes have the disadvantage of fragility and they are difficult to connect to other components. The latter can be minimized by using special joints but repairs in the field are made much more difficult.

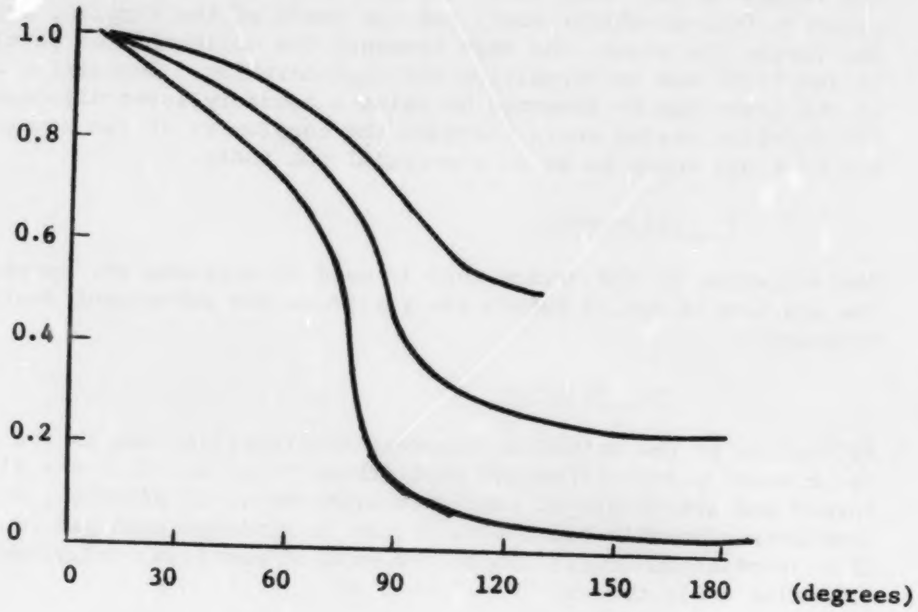

FIGURE J-1

__Angle Between Nozzle and Wind Direction__

A glass-lined Vycor stainless steel probe combined the advantage of strength of the one and corrosion resistance of the other. However, breakage of the glass-lined steel probes due to thermal or mechanical stresses coupled with its high initial cost imposes considerable hardship on the users.

The length of the probe will vary and will be determined by the stack diameter (six-to-thirty feet) and the needs of the sampling program. The longer the probe, the more tendency for collection of particulates in the probe due to deposition and agglomeration. Deposition of particles in the probe can be lessened by using a boundary layer dilution probe. The dilution system would increase the complexity of the sampling system and none are known to be in commercial use today.

3. Collectors

The collector is the device that is used to separate the particles from the gas sample and to retain the particles for subsequent analyses or treatments.

a. Filters

Filtration is the method of broadest applicability and is the most used for mineral particulates and soot (those particles that are already formed and are stable at stack temperatures). In practice, a cyclone is sometimes placed in front of a filter to minimize problems of plugging. This practice generally limits the size of particles collected by the filtering media to less than 3 to 5 μm.

A wide variety of filter media are available permitting selection based upon factors such as filtration efficiency, pressure drop per unit flow, inertness, composition (glass, cellulose, alundum-refractory, asbestos, polymeric materials) low background contamination (for special analytical needs), color, solubility, thermal stability, price, etc. The efficiency of a filter generally improves with the accumulation of collected material but eventually the resistance can become so great that adequate gas passage is impaired.

Filter media may be paper, glass fiber, alundum, cloth, membrane, etc., with the material selected being that best suited to sampling conditions, collecting efficiency desired and analytical procedures to be followed. Paper, glass fiber, and alundum (aluminum oxide) are used extensively for thimbles. The alundum filter has the advantage of being able to withstand temperatures of over 1000°F. Both the alundum and glass fiber filters are relatively non-hydroscopic and require less time for humidity conditioning prior to weighing than cellulose filter media. Filter media can be used over a wide range of sampling rates and, if properly selected, perform very satisfactorily. Membrane filters collect the particulate matter on a flat surface which can then be examined microscopically. They are used extensively for particle size determination. They are restricted to relatively low sampling rate systems, e.g., liters per minute rather than cubic feet per minute. Furthermore, they are limited to low temperature applications. The 47 mm size is about as large as is commonly used in this application and the cost of membrane filters is still considerably more than other media.

Cloth is used infrequently as a collecting medium as it is inferior to other materials for small particle collection. However, it has some application in large high-volume systems.

Filters can be placed either inside or outside of the stack. The former introduces difficulties due to temperature and an increased potential for reaction between the collected material and the gas stream. The latter introduces errors due to sampling lines losses. In general, a drop in temperature to 300°F to 250°F (via cooling of the gas) and placing the filter outside will reduce the magnitude of chemical changes in the sample during the collection step—especially if organics and condensibles are involved. On the other hand, this same step (lowering the temperature) increases the likelihood of hydration and other forms of chemical reaction occuring with the mineral particulates.

A further more detailed discussion of high efficiency glass fiber filters is given in Appendix G.

b. Classifiers

A classifier is a device which separates particulates into one or more size fractions. One type, the cyclone, is used before the main collection device (filter or impinger) to minimize overloading and plugging, which can cause loss of sample and changes in flow rate. Cascade impactors, such as the Anderson sampler, also is a type of classifier. This is a multijet, multistage impactor which collects weighable quantities of particulate matter. High efficiency is reported for submicron particles and above. The practical upper limit of size is < 50μ. These impactors generally must be operated at constant flow rates, have very low capacity, and are much more expensive than a cyclone.

Cyclone collectors are used extenstively as a precollector or classifier unit in a sampling system. Cyclones are efficient above a minimum particle size; some commercial designs operate down to a 3 μm cutoff and research sampling devices are designed to submicron cutoffs. They are relatively inexpensive and have no moving parts to wear out, can be used both inside and outside the stack, and they can be obtained in sizes and capacities from a few liters per minute up to a number of cubic feet per minute.

If the gas stream contains water droplets, those larger than the cutoff size will be collected by the cyclone along with the particulates. This can cause great difficulty if it is desired to use a cyclone for collection of particulates for characterization. Probably all one can do is to collect the "mud", dry it and weigh the residue. Possibilities for prior interactions with the water (chemical reactions, hydration, decomposition) are too high to make individual particle characterization meaningful.

The cyclone can be placed either inside or outside of the stack. When placed inside right after the nozzle, it should minimize particle losses in the probe (due to gravitational and turbulent deposition mechanisms) by removing large particles immediately. Because the particulates fall out of the main stream during collection in a cyclone, and thus are collected primarily out of the flow of the gas, there should be little interaction with the gas stream itself (if dry). Decomposition of the sample after collection in a cyclone, due to longer residence in the stack is a possibility, but may not be serious since the sample probably has been exposed to much higher temperatures in the incinerator fire box (1000-2200°F). The rate of chemical reactions of the gases after cooling to stack temperature should be considerably lower. Combustion and pyrolysis may still be a problem, however, for organic compounds and carbon particles especially where the stack gas is very hot. An extra advantage of a cyclone inside the stack wall is that the pressure drop across the cyclone can be employed as a flow measurement at stack conditions.

When placed outside, the chances for chemical decomposition (or reaction) are reduced--especially if the stack gases are cooled first. However, the advantages derived from the ability to measure flow at stack conditions and the removal of large particulates before entering the probe will have been lost.

A possible solution to the problems associated with handling a wet gas stream in a cyclone is to dilute the flue gases ahead of the cyclone. This would get the dew point of the gas stream to a point where liquid would not collect in the cyclone. It would not solve the situation where water droplets were already present before dilution.

As to materials of construction, the same problems would apply here as with the nozzle and probe.

c. Impactors/Impingers

A number of collectors are based on impaction. When the particles are collected on a target submerged in a liquid, the device is called an impinger although it is essentially a single stage impactor. Impingers have a possible advantage in that they collect gases too. Disadvantages, of course, are caused by solubility, evaporation of the collecting liquid and the nuisance factor introduced by the requirement to handle liquids in the field (freezing, spilling, etc.)

The wet impingement device used is usually the Greenburg-Smith impinger with the collecting liquid being initially distilled water. In the Greenburg-Smith impinger gas is drawn through an orifice 2.3 mm in diameter at a rate of approximately 1 cfm (0.028 m^3/min) and impinged against a flat surface 5 mm distant. The particles are retained in liquid which fills the impinger flask to a depth of about 2 inches.

When an impinger contains a liquid, it can become a very efficient collector for aerosol particles, very fine (submicron)particles, condensibles (organic and inorganic) and soluble gases. Sometimes the impinger catch is thought to be synonymous with condensibles but clearly that is not necessarily the case since there is a high likelihood that gases dissolve as well as condense in the impinger solution. The impinger can contain water (either purposely or as a result of condensation), a reactive solution (such as sodium hydroxide), and organic solvent (such as an alcohol or benzene), or a dry solid (such as silica, charcoal or alumina). In some situations, a filter can be placed after the impinger to ensure collection of aerosol or entrained particles.

The impinger is usually operated at ambient temperature or less within the limits of the properties of the collecting liquid. The lower the temperature, the more efficient the collection efficiency for the so-called condensibles.

d. Other

Electrostatic precipitation is also used for particle sampling. This well known method passes particles through a charging section and then precipitates the charged particles in an electric field. High efficiency performance is easily attained even for small particles. The pressure drop across a precipitator is low since there is little to obstruct the flow. A high voltage power supply is required and presents a safety hazard. Furthermore, collection efficiency is dependent upon particle properties (size, dielectric properties) which makes it independable in variable situations such as incinerator sampling.

The principal of thermal precipitation has been exploited in a classical air sampling instrument and is still used extensively in research applications but generally not in field work. The thermal precipitation forces are very gentle and liquid droplets or fragile agglomerates are not likely to shatter when they contact the collecting surface. Furthermore, they are very efficient for submicron particles and have found use for collecting low vapor pressure and fogs. The original instruments were limited severely by a low sampling rate (10 cc/min). Other units have been designed which employ high flow rates and time resolution of the sample. Due to the high degree of control required and the potentially low efficiency, they are not practical for incinerator sampling.

Particles can also be collected by gravitational sedimentation upon horizontal surfaces. Devices have been constructed of stacks of closely spaced horizontal plates to minimize the sedimentation distance and increase the gas feed rate. Small units have been used as collectors in atmospheric sampling. They are, however, extremely slow and bulky since the unit must be designed for viscous flow, and the residence time must be sufficient to allow sedimentation. They are not considered appropriate for incinerator sampling.

4. Flow Meter

In particulate stack sampling, two types of sample gas metering are employed:

(1) gas flow, $\left(\frac{d\ (\text{volume})}{dt}\right)$

(2) volume, (integrated flow)

A well-designed sampling system will have one of each type. The flow meter is used in adjusting flow to isokinetic conditions (a null nozzle may be considered to satisfy the function of the flow meter), while the gas volume meter is used for calculating particulate concentrations and emissions. The accuracy of a concentration (hence, emission) determination depends as much upon the accuracy of sample gas volume measurements as upon accuracy of particulate mass. This may be seen in equation (1) below:

$$C = \frac{M}{V\left(\frac{P_m}{P_{std}} \times \frac{T_{std}}{T_m}\right)} \qquad (1)$$

where: C = particulate mass concentration

M = mass of collected particulates from a sample

V = volume of sample gas measured by the meter

P_m = absolute pressure of the sample gas at the meter

P_{std} = standard pressure

T_m = absolute temperature of the sample gas at the meter

T_{std} = standard temperature

It can also be seen from equation (1) the the accuracy of C also depends in a first order manner, on the measurement of sample gas temperature and pressure at the meter. It is easy to measure the gas temperature within less than one percent. When the gas meter is located upstream of the pump the meter must be leak free. The meter may be operated at a few inches of mercury vacuum and the pressure must be measured with an error of less than 0.3 inches of mercury for a concentration error of less than one percent. Most reasonably priced mechanical vacuum gauges are not this good when the vacuum is less than about 5 inches of mercury. For this reason, any gas meter operated in this vacuum range should be equipped with a mercury manometer or a high quality mechanical gauge. Most gas meters are not rated to operate under more than about 1" Hg vacuum. When the meter is downstream of the pump (the pump must be leak-free), the meter pressure is virtually barometric and hence not likely to introduce a significant error.

The required accuracy of a gas meter depends on its use. A flow meter used in adjusting isokinetic flow need not be as accurate as a meter used in measuring sample volume. Small discrepancies from isokinetic flow do not affect the accuracy of results as significantly as errors in volume measurement. Within accuracy constraints, the particular gas meter(s) must be in harmony with the total sampling system and within the general engineering requirements of:

(1) Portability

(2) Operational simplicity

(3) Reliability/stability

(4) Ruggedness

Types of gas meters are summarized in Table J-1.

The present state-of-the-art uses mainly the dry gas meter and calibrated orifices with the calibrated cyclone used to a lesser extent. These are time-tested techniques which will provide the necessary results, although it seems that modern technology could be used to improve or replace some of these techniques. An example would be to use electronic analog devices with a calibrated cyclone to provide volume as well as flow measurement. Also, a permanent record (strip chart) could be produced to reduce the possibility of human error of reading gauges.

5. Pumps

Suction sources may consist of a variety of motor-driven pumps or air ejectors.

The rotary vacuum pump is a positive displacement unit utilizing vanes of graphite or fiber providing pulse-free flow at a low initial cost and low maintenance cost. These units are available in lubricated or oil-less types with a wide range of volume and pressure characteristics from several commercial sources.

The cycloid pump is also a positive displacement unit which provides pulse-free flow. It has the disadvantage of being unable to pull as great a vacuum as the rotary vane type pump due to slippage between the cycloids. It is more expensive.

Diaphragm pumps, usually smaller than the previously described suction sources, are used in sampling operations. These pumps do not operate under high pressures of vacuum.

TABLE J-1

Summary of Gas Meters

Meter	Type	Use In Particulate Stack Sampling	Common Capacity	Typical Best Accuracy	Reliability Stability	Operational Simplicity	Portability	Ruggedness	Remarks
Dry gas Meter	Volume	Very Common	.1 to several cfm	∼1	Check cal. frequently	Good	Good	Good	Direct reading
Calibrated Orifice Meter	Flow	Very Common	Any	1-2%	Good	Good	Good	Good	ΔP output
Rotameter	Flow	Occational	<a few cfm	∼1	Good	Fair (leveling required)	Good	Fair	Usually required cal bration curves for reading
Wet Test Meter	Volume	Not common now	<∼1 cfm	0.5%	Good	Poor	Poor	Poor	Direct reading
Rotary Gas Meter (Root Type)	Volume	Not common	>∼1 cfm	∼1%	Good	Good	Poor (heavy)	Good	A good calibration instrument
Turbine Meter	Volume or Flow	Not common	<1 cfm to several cfm	2-5%	Good	Good	Can be made good	Fair (electronic equipment)	Recorder output possible
Venturi Meter	Flow	Not common	Any	1-2%	Good	Good	Good	Good	ΔP output
Mass Flow Meter	Mass Flow or Total Mass	Not common	∼1 cfm	∼2%	Good	Good	Can be made good	Fair (electronic equipment)	Temp. & pressure correction not necessar Recorder output possible
Calibrated Cyclone	Flow	Common	Any	Expect ∼1-2%	Good	Good	Good	Good	Make use of an existing component. ΔP output

Centrifugal pumps (compressors) are often used in sampling systems where a large volume of flow is required at low head.

Ejectors may be used over a wide range of volumes and are capable of operating at relatively large pressure drops. Compressed air or steam requirements and noise are the two greatest problems in the use of ejectors. Their use is minimal.

6. Supporting Element

Measurements to establish gas velocity and calculate gas volume are usually made with a Pitot-static tube and an inclined manometer. These measurements are used to determine isokinetic velocity and are an important factor in the accuracy of a sampling procedure.

A special "S" type "Staubscheibe" tube is frequently used on dirty or wet gases. The advantage of this unit is that it does not plug as readily as the conventional Pitot-static tube which has extremely small openings (0.040 in. static ports), and thus lessens the chance for large errors due to plugging.

A correction factor must be applied to all velocity measurements made with the "S" type tube. The factor can be determined by calibration with a Pitot-static tube. Gas velocity as calculated from the "S" type tube reading must be multiplied by the correction factor to obtain the true gas velocity. Pre-calibrated units are available from manufacturers.

Velocity pressures are indicated on an inclined manometer which is usually constructed to read up to two or more inches of water in increments of 0.01 inches.

Static pressure readings are also an important part of the supporting sample data. Static pressure readings are usually obtained by using the static pressure holes in the Pitot-static tube connected to the draft gauge with the other tap of the gauge open to the atmosphere.

Alternatively, the static pressure is often measured with a water U-tube manometer connected to tubing flush with the inside wall of the duct. Instruments for temperature measurement are largely governed by the temperature found and the frequency of measurement desired.

Dial thermometers and thermocouples with a potentiometer are frequently used and provide suitable data.

Determination of the moisture content of the sample requires the condensation of excess moisture at the sampling temperature and the immediate measurement of the volume of gas at saturated conditions. Condensation at ambient or a controlled temperature is achieved by condensing coils or by passing the gas through a temperature controlled chamber where the condensed water can be subsequently measured.

The moisture content in the stack gas can be determined from wet and dry bulb temperature readings by use of the following formula:

$$p = p' - 0.01\ (t_d - t_w)$$

where p = vapor pressure of gas in inches of mercury

p' = vapor pressure of saturated gas at t_w in inches of mercury

t_d = dry bulb temperature in degrees F

t_w = wet bulb temperature in degrees F

$$\%\ H_2O = \frac{p}{(p_b \pm p_s)} \times 100$$

p_b = barometric pressure in inches of mercury

p_s = stack pressure in inches of mercury

In many sampling operations, the density of the gas may be assumed to be the same as air and no actual evaluation or correction made. Gas density can be measured by the Shilling or National Bureau of Standards Gas Density Apparatus. As these instruments are not usually available, the most commonly used method employs the Orsat gas analysis technique to measure composition to permit calculation of molecular weight gas density.

In the Orsat gas analysis, CO_2, CO, and O_2 are determined by reaction with appropriate reagents and the remaining volume of the original sample is considered to be nitrogen. From the gas composition and known molcular weights, the density of the sampled gas can be determined.

Data on CO_2 and O_2 content are also required for statement of emissions on a normalized basis.

The Orsat instrument is basically a laboratory device and does not function well in the field, nor does it lend itself well to operation by the inexperienced chemist or technician. Instruments are now on the market to make volumetric (%) evaluations of CO_2 and O_2 rapidly and directly from the stack or sampled gas much more easily and rapidly than the Orsat and the equipment lends itself well to use under field conditions.

APPENDIX K

METHOD 5 - DETERMINATION OF PARTICULATE EMISSIONS FOR STATIONARY SOURCES*

Definition of Particulate

Particulate matter is defined as "any finely divided liquid or solid material, other than uncombined water, as measured by Method 5."

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. Apparatus

2.1 Sampling Train. The design specifications of the particulate sampling train used by EPA (Figure K-1) are described in APTD-0581. Commercial models of this train are available.

2.1.1 Nozzle. Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe. Pyrex (trade name) glass with a heating system capable of maintaining a minimum gas temperature of 250°F at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft) are encountered at temperatures less than 600°F Incoloy 825 (trade name) or equivalent, may be used. Probe for sampling gas streams at temperatures in excess of 600°F must have been approved by the Administrator.

2.1.3 Pitot Tube. Type S or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder. Pyrex (trade name) glass with heating system capable of maintaining minimum temperature of 225°F.

2.1.5 Impingers/Condenser. Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a 1/2-inch ID glass tube extending to one-half inch from the bottom of the flask. The second

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*Taken from "Standards of Performance for New Stationary Sources," Federal Register, Vol. 36, No. 247, Thursday, December 23, 1971, p. 24888.

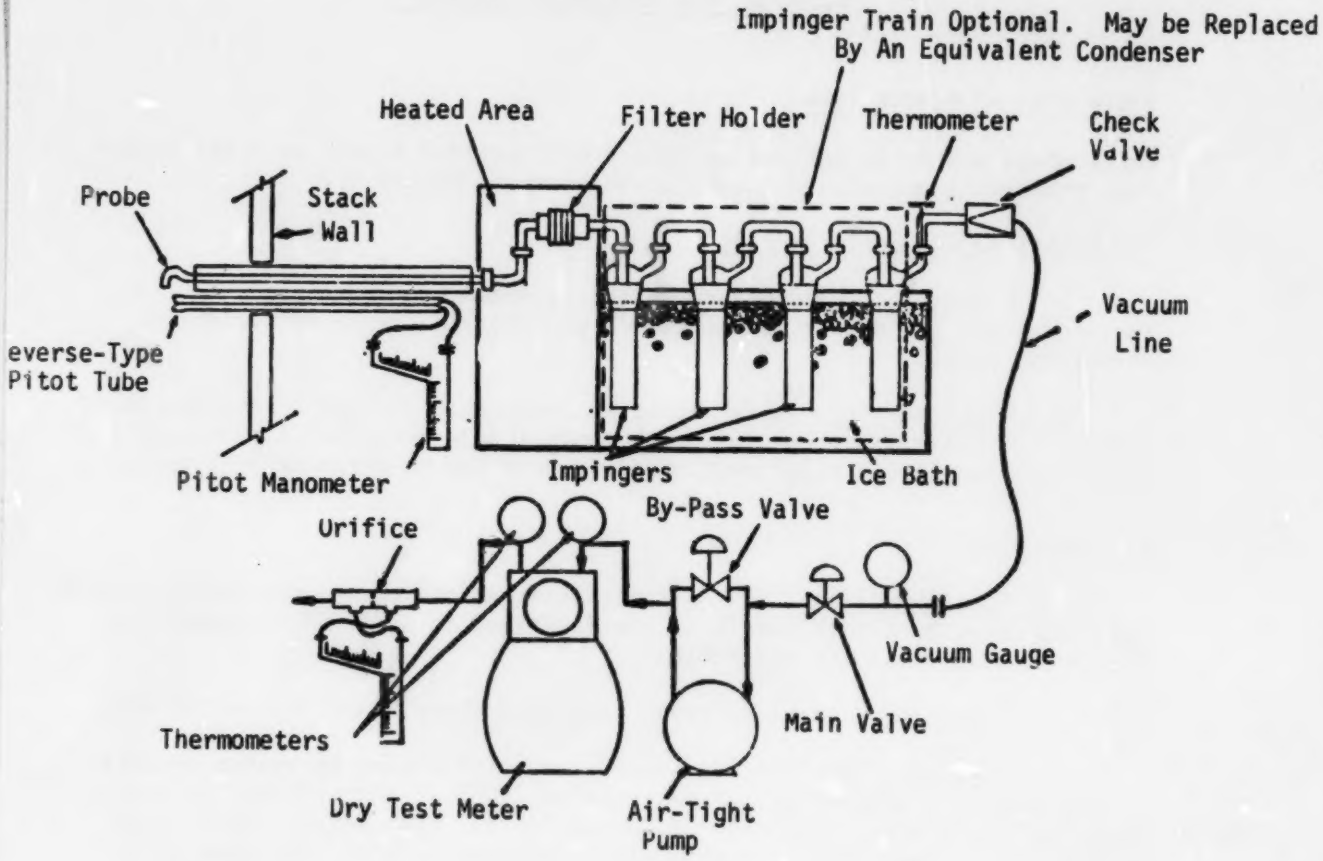
Impinger Train Optional. May be Replaced By An Equivalent Condenser
Heated Area
Filter Holder
Thermometer
Check Valve
Probe
Stack Wall
Vacuum Line
everse-Type Pitot Tube
Pitot Manometer
Impingers
Ice Bath
Orifice
By-Pass Valve
Vacuum Gauge
Main Valve
Thermometers
Dry Test Meter
Air-Tight Pump

FIGURE K-1

Particulate Sampling Train

impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5°F, dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer. To measure atmospheric pressure to ± 0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe Brush. At least as long as probe.

2.2.2 Glass Wash Bottles. Two

2.2.3 Glass Sample Storage Containers.

2.2.4 Graduated Cylinder. 250 ml.

2.3 Analysis.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to ± 0.1 mg.

2.3.4 Trip Balance. 300 g capacity, to measure to ± 0.05 g.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber, MSA 1106 BH (trade name) or equivalent, numbered for identification and preweighed.

3.1.2 Silica Gel. Indicating type, 6-16 mesh, dried at 175°C (350°F) for 2 hours.

3.1.3 Water.

3.1.4 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Acetone. Reagent grade.

3.3 Analysis.

3.3.1 Water.

3.3.2 Dessicant. Drierite (trade name) indicating.

4. Procedure

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of Collection Train. Weigh to the nearest gram approximately 200 g of silica gel. Label a filter of proper diameter, desiccate (dry using Drierite at 70°F ± 10°F) for at least 24 hours and weigh to the nearest 0.5 mg in a room where the relative humidity is less than 50%. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure K-1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250°F at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70°F or less. Temperatures about 70°F may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate Train Operation. For each run, record the data required on the example sheet shown in Figure K-2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusions of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in Section 4.2.

4.2 Sample Recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Plant ____________
Location ____________
Operator ____________
Date ____________
Run No. ____________
Sample Box No. ____________
Meter Box No. ____________
Meter ΔH ____________
C Factor ____________

SCHEMATIC OF STACK CROSS SECTION

Ambient Temperature ____________
Barometric Pressure ____________
Assumed Moisture,% ____________
Heater Box Setting ____________
Probe Length,m ____________
Nozzle Diameter,in ____________
Probe Heater Setting ____________

Traverse Point Number	Sampling Time (e), min.	Static Pressure (P_S) in. Hg	Stack Temperature (T_S) °F	Velocity Head (ΔP_S)	Pressure Differential Across Orifice Meter (ΔH) in. H_2O	Gas Sample Volume (Vm) ft^3	Gas Sample Temperature at Dry Gas Meter		Sample Box Temperature (°F)	Temperature Of Gas Leaving Condenser or Last Impinger (°F)
							Inlet ($Tm_{in.}$)°F	Outlet (Tm_{out})°F		
							Avg.	Avg.		
							Avg.			

FIGURE K-2. Particulate Field Data

Reproduced from best available copy.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure K-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. Calibration

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. Calculations

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure K-2).

6.2 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (70°F, 29.92 inches Hg) by using Equation K-1.

$$Vm_{std} = Vm\left(\frac{Tstd}{Tm}\right)\left(\frac{Pbar + \frac{\Delta H}{13.6}}{Pstd}\right) =$$

$$\left(17.71\ \frac{°R}{In.\ Hg}\right) Vm \left(\frac{Pbar + \frac{\Delta H}{13.6}}{Tm}\right)$$

equation K-1

Plant ___________

Date ___________

Run No. ___________

Container Number	Weight of Particulate Collected, mg		
	Final Weight	Tare Weight	Weight Gain
1			
2			
Total	☒	☒	

	Volume of Liquid Water Collected		
	Impinger Volume, ml	Silica Gel Weight, g	
Final			
Initial			
Liquid Collected			
Total Volume Collected		g*	ml

Convert Weight of Water to Volume by Dividing Total Weight Increase by Density of Water (1 g ml):

$$\frac{\text{Increase, g}}{(1\ \text{g/ml})} = \text{Volume Water ml}$$

FIGURE K-3. Analytical Data

where:

Vm_{std} = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

Vm = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

Tm = Average dry gas meter temperature, °R.

$Pbar$ = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of Water Vapor.

$$Vw_{std} = Vl_c \left(\frac{\rho H_{2o}}{MH_{2o}}\right)\left(\frac{RTstd}{Pstd}\right) = \left(0.0474 \frac{\text{cu. ft.}}{\text{ml}}\right) Vl_c$$

equation K-2

where:

Vw_{std} = Volume of water vapor in the gas sample (standard conditions), cu. ft.

Vlc = Total volume of liquid collected in impingers and silica gel (see Figure K-3) ml.

ρH_{2o} = Density of water, 1 g/ml.

MH_{2o} = Molecular weight of water, 18 lb/lb-mole.

R = Ideal gas constant, 21.83 inches Hg - cu. ft./lb-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530°R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture Content.

$$B_{wo} = \frac{Vw_{std}}{Vm_{std} + Vw_{std}}$$

equation K-3

where:

B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

Vw_{std} = Volume of water in the gas sample (standard conditions), cu. ft.

Vm_{std} = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total Particulate Weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure K-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154 \frac{\text{gr.}}{\text{mg.}}\right)\left(\frac{M_n}{Vm_{std}}\right)$$

equation K-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

Vm_{std} = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453{,}600}\ \frac{\text{lb}}{\text{mg.}}\ M_n\right)}{Vm_{std}} = 2.205 \text{ X } 10^{-6}\ \frac{M_n}{Vm_{std}}$$

equation K-5

where:

c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis.

453,600 = Mg/lb.

M_n = Total amount of particulate matter collected, mg.

Vm_{std} = Volume of gas sample through dry gas meter (standard conditions) cu. ft.

6.7 = isokinetic variation.

$$I = \frac{\left[\frac{Vl_c(\rho H_2O)R}{MH_2O} + \frac{Vm}{Tm}\left(Pbar + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \text{ X } 100$$

$$= \frac{\left(1.667\frac{\text{min.}}{\text{sec.}}\right)\left[\left(0.00267\frac{\text{in. Hg-cu.ft.}}{\text{ml.-°R}}\right) Vl_c + \frac{Vm}{Tm}\left(Pbar + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n}$$

equation K-6

where:

I = Percent of isokinetic sampling.

Vl_c = Total volume of liquid collected in impingers and silica gel (see Fig. K-3) ml.

ρH_2O = Density of water, 1 g./ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb. mole-°R.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure K-2) °R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Fig. K-2), inches Hg.

T_s = Absolute average stack gas temperature (see Fig. K-2), °R.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft/sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross-sectional area of nozzle, eq. ft.

6.8 Acceptable Results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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16. ABSTRACT

Municipal incinerators, and similar stationary sources, though contributing only a few percent of the total national air pollution load, are important sources of pollution near population centers. The particulate matter they emit has a significant adverse effect on health, on materials of construction and on visibility; they are responsible for many complaints. Therefore, the Federal Government, through the Environmental Protection Agency, has promulgated standards that specify the permissible levels of particulate matter emitted from newly constructed incinerators operating at or above a charging rate of 50 tons per day. In many cases, however, the chemistry of the particulate species present in these emissions is not well know. Consequently, there is a need to define more thoroughly the chemical nature of particulate emissions from incinerators and to gain a better understanding of how the sample collection equipment used by the EPA influences the physical and chemical properties of the particulate. The primary goal of the program has been to help develop the data base and the technology which will permit representative measurements of source particulate emissions to be obtained from waste incineration sources, and from the particulate pollution control devices associated with such sources.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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